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CHEMICAL KINETICS

EXERCISE 1 JEE MAIN/BOARDS

Q.1 A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the reaction A + B = C occurs. At the end of 1h, A is 75%t reacted. How much of A will be left unreacted at the end of 2h if the reaction is (a) first order in A and zero order in B; (b) first order in both A and B; and (c) zero order in both A and B?

Q.2 The reaction

$CH_3–CH_2–NO_2 + OH^- \longrightarrow CH_3–CH–NO_2^- + H2O$

obeys the rate law for pseudo first order kinetic in the presence of a large excess of hydroxide ion . If 1% of nitro ethane undergoes reaction in half minute when the reaction concentration is 0.002 M, What is the pseudo first order rate constant?

Q.3 The decomposition of a compound P at temperature T according to the equation

$$2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$$

is the first order reaction After 30 minutes from the start of decomposition in a closed vessel the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minute, if volume of liquid S is supposed to be negligible Also calculate the tiny fraction $t_{1/8}$

Given. Vapor pressure of S (ℓ) at temperature T = 32.5 mm Hg.

Q.4 A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At t = 0. the volume of the reagent consumed is 25 ml and at t = 10 min, the volume used up is 32 ml. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

Q.5 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open Due to this, some H_2O_2 decomposed To determine the new volume strength after 6 hours. 10 mL of this solution was diluted to 100 mL 10mL of this diluted solution was titrated against 25mL of 0.025 M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2.

Q.6 A metal slowly forms an oxide film which completely protects the metal when the film thickness is 3.956 thousand times of an inch. If the film thickness is 1.281 thou. in 6 weeks, how much longer will it be before it is 2.481 thou.? The rate of film formation follows first order kinetics.

Q.7 An optically active compound A upon acid catalyzed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was – 20°. If optical rotation per mole of A, B & C are 60°,

40° & – 80°. Calculate half-life of the reaction.

Q.8 A vessel contains dimethyl ether at a pressure of 0.4atm.Dimethyl ether decomposes as

$CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$. The rate constant of decomposition is 4.78×10^{-3} min^{-1}. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition.

Q.9 At room temperature (20°C) orange juice gets spoilt in about 64 hours. In a refrigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice (b) How long should it take for juice to get spoilt at 40°C?

Q.10 A first order reaction, A → B, requires activation energy of 70 kJ mol^{-1} When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature.

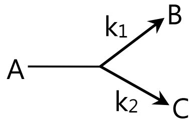
Q.11 Two reactions

(i) A → products

(ii) B → products,

follow first order kinetics The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy- of activation for the reaction (ii) is half that of reaction (i). Calculate the rate constant of the reaction (ii) at 300 K

Q.12 A certain organic compound A decomposes by two parallel first order mechanism



If $k_1 : k_2 = 1 : 9$ and $k_1 = 1.3 \times 10^{-5} s^{-1}$.
Calculate the concentration ratio of C to A, if an experiment is started with only A and allowed to run for one hour

Q.13 The reaction cis – $Cr(en)_2(OH)_2^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ trans– $Cr(en)_2(OH)_2^+$ is first order in both directions At 25°C the equilibrium constant is 0.16 and the rate constant k_1 is $3.3 \times 10^{-4}\ s^{-1}$. In an experiment starting with the pure cis form, how long would it take for half the equilibrium amount of the Trans isomer to be formed?

Q.14 For a reversible first-order reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

$k_1 = 10^{-2}\ s^{-1}$ and $[B]_{eq}/[A]_{eq} = 4$. If $[A]_0 = 0.01$ mole L^{-1} and $[B]_0 = 0$, what will be the concentration of B after 30 s?

Q.15 For the system A(g) 1 B(g), ΔH for the forward reaction is –33kJ/mol (Note. ΔH = ΔE in this case).
Show that equilibrium constant

$K = \frac{[B]}{[A]} = 5.572 \times 10^5$ at 300 K. If the activation energies E_r & E_b are in the ratio 20: 31. Calculate E_r and E_b at this temperature .Assume that the pre-exponential factor is the same for the forward and backward reactions

Q.16 The complex $[Co(NH_3)_5F]^{2+}$ reacts with water according to the equation
$[Co(NH_3)_5F]^{2+} + H_2O \rightarrow [Co(NH_3)5(H_2O)]^{3+} + F^-$

The rate of the reaction = rate const. x$[complex]^a$ x$[H^+]^b$. The reaction is acid catalysed i.e. $[H^+]$ does not change during the reaction.
Thus rate = $k[Complex]^a$
where $k' = k[H^+]^b$ calculate 'a' and 'b' given the following data at 25°C.

[Complex]M	$[H^+]$M	$T_{1/2}$hr	$T_{3/4}$hr
0.1	0.01	1	2
0.2	0.02	0.5	1

Q.17 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E′ for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by $E' = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$

Q.18 For the mechanism

$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C\ ;\ C \xrightarrow{k_3} D$

(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.
(b) Assuming that $k_3 << k_2$, express the pre-exponential factor A and E_a for the apparent second order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2}, and E_{a3} for the three steps.

Q.19 The reaction of formation of phosgene from CO and Cl_2 is $CO + Cl_2 \longrightarrow COCl_2$
The proposed mechanism is

(i) $Cl_2 \underset{k-1}{\overset{k_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium)

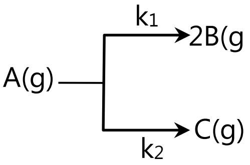
(ii) $Cl + CO \underset{k-2}{\overset{k_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

(iii) $COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$ (slow)

Show that the above mechanism leads to the following rate law $\frac{d[COCl_2]}{dt} = K[CO][Cl_2]^{3/2}$.

Where $K = k_3 \cdot \frac{k_2}{k-2}\left(\frac{k_1}{k-1}\right)^{1/2}$.

Q.20 For the following first order gaseous reaction



The initial pressure in a container of capacity V litres is 1 atm. Pressure at tune t = 10 sec is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reaction.

Q.21 A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion?

Q.22 The specific rate constant for a reaction increases by a factor 4, of the temperature is changed from 27°C to 47°C. Find the activation energy for the reaction

Q.23 The reaction $2A + B + C \longrightarrow D + 2E$ is of first order with respect to A. of second order with respect to B and is of zero order with respect to C

(i) Write down the rate law for the reaction

(ii) What will be the effect of doubling concentration of A. B and C.

Q.24 A first order reaction is 50% completed in 30 min at 27°C and in 10 minutes at 47°C. Calculate the rate constant at 27°C and the energy- of activation of the reaction in kJ per mole

Q.25 The optical rotation of sucrose in 0.5 M HCl at 35° C at different time intervals are given below. Show that the reaction follows first order kinetics

Time (min)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	–11.1

Q.26 $t_{1/2}$ of a reaction is halved as the initial concentration of the reaction is doubled, find out the order of the reaction.

Q.27 The rate constant of a reaction is $1.5 - 10^{-7}$ sec^{-1} at 50°C and 4.5×10^{-7} sec^{-1} at 100°C. Evaluate the Arrhenius parameters A and Ea.

Q.28 A substance reacts according to the law of firs: order reaction the velocity constant of the reaction is 1.0×10^{-2} sec^{-1}. If initial canc. of the substance is 1.0 M

(a) Find out the initial rate

(b) Find out the rate after 1 min.

Q.29 What will be initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and concentration of reactant is 0.2 mol dm^{-3}. How much of reactant will be converted into products in 200 minutes.

Q.30 A first order reaction is 20% complete in 10 minutes. Calculate

(a) Specific rate constant of the reaction and

(b) Time taken for the reaction to go to 75 % completion

EXERCISE 2 JEE MAIN

Q.1 For the reaction $A + B \longrightarrow C$; starting with different initial concentration of A and B, initial rate of reaction were determined graphically in four experiments._

S. No.	$[A]_0$/M (Initial conc.)	$[B]_0$/M (Initial conc.)	rate/ (M sec^{-1})
1	1.6×10^{-3}	5×10^{-2}	10^{-3}
2	3.2×10^{-3}	5×10^{-2}	4×10^{-3}
3	1.6×10^{-3}	10^{-1}	2×10^{-3}
4	3.2×10^{-3}	10^{-1}	8×10^{-3}

Rate law for reaction from above data is

(A) $r = k[A]^2W^2$ (B) $r = k[A]^2[B]$

(C) $r = k[A][B]^2$ (D) $r = k[A][B]$

Q.2 The rate law for a reaction between the substances A and B is given by rate = $k[A]^n[B]^m$ On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as

(A) $2^{(n-m)}$ (B) $1/2^{m+n}$

(C) $(m + n)$ (D) $(n - m)$

Q.3 In a first order reaction, the concentration of the reactant, decreases from 0.8 to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is

(A) 30 minutes (B) 15 minutes

(C) 7.5mnutes (D) 60 minutes

Q.4 The rate equation for the reaction $2A + B \longrightarrow C$ is found to be: rate=k [A] [B] The correct statement in relation to this reaction is

(A) Unit of k must be s^{-1}

(B) $t_{1/2}$ is a constant

(C) Rate of formation of C is twice the rate of disappearance of A

(D) Value of k is independent of the initial concentration of A and B

Q.5 $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to 3/4 of its value. If the rate constant for a first order reaction is k, the $t_{1/4}$ can be written as [In2 = 0.695, In = 1.1]

(A) 0.69/k (B) 0.75/k

(C) 0.10/k (D) 0.29/k

Q.6 A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will

(A) Double (B) Remain unchanged

(C) Triple

(D) Increase by a factor of 4

Q.7 For a hypothetical reaction,

$A + 3B \rightarrow P \quad \Delta H = -2x$ kJ/mole of A

& $M \rightarrow 2Q + R \ \Delta H = -x$ kJ/mole of M

If these reactions are carried simultaneously in a reactor such that temperature is not changing. If rate of disappearance of B is y M sec^{-1} then rate of formation (in M sec^{-1}) of Q is:

(A) $\frac{2}{3}y$ (B) $\frac{3}{2}y$

(C) $\frac{4}{3}y$ (D) $\frac{3}{4}y$

Q.8 Gaseous reaction $A \longrightarrow B + C$ follows first order kinetics. Concentration of A changes from 1M to 0.25 M in 138.6 minutes. Find the rate of reaction when concentration of A is 0.1 M.

(A) 2×10^{-3}M min^{-1} (B) 10^{-3}M min^{-1}

(C) 10^{-4}M min^{-1} (D) 5×10^{-4}M min^{-1}

Q.9 The initial rate of zero-order reaction of the gaseous reaction $A(g) \longrightarrow 2B(g)$ is 10^{-2} M min^{-1}. If the initial concentration of A is 0.1M. What would be the concentration of B after 60 sec?

(A) 0.09 M (B) 0.01 M

(C) 0.02 M (D) 0.002 M

Q.10 Consider the following first order competing reactions:

$X \xrightarrow{k_1} A + B$ and $Y \xrightarrow{k_2} C + D$

if 50% of the reaction of X was completed when 96% of the reaction of Y was completed the ratio of their rate constants (k_2/k_1) is

(A) 4.06 (B) 0.215

(3) 1.1 (D) 4.65

Q.11 At certain temperature, the half life period for the thermal decomposition of a gaseous substance depends on the initial partial pressure of the substance as follows

P(mm Hg) 500 250

$t_{1/2}$(in min) 235 950

Find the order of reaction

[Given log(23.5) = 1.37; log (95)= 1.97; log 2 = 0.30]

(A) 1 (B)2 (C) 2.5 (D)3

Q.12 Consider the reaction: $A \longrightarrow B + C$

Initial concentration of A is 1M. 20 minutes time is required for completion of 20% e reaction.

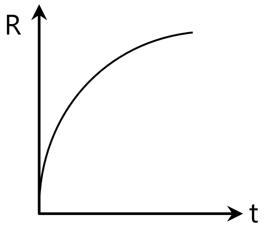
If = $\frac{d[B]}{dt}$ k[A], then half life ($t_{1/2}$) is

(A) 55.44 min (B) 50 min

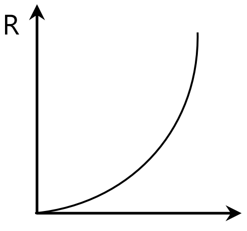
C) 62.13 min (D) None of these

Q.13 If decomposition reaction $A(g) \longrightarrow B(g)$ follows first order kinetics then the graph of rate of formation (R) of B against time t will be

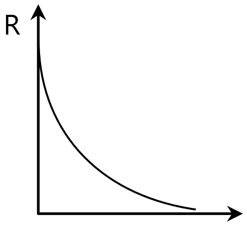
(A)



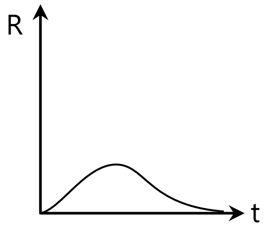
(B)



(C)



(D)



Q.14 The rate constant for the forward reaction $A(g) \longrightarrow 2B(g)$ is $1.5 \times 10^{-3}\ s^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

(A) 1.50×10^{4}L mol^{-1} s^{-1}

(B) 1.5×10^{11}L mol^{-1} s^{-1}

(C) 1.5×10^{10}L mol^{-1} s^{-1}

(D) 1.5×10^{-11}L mol^{-1} s^{-1}

Q.15 Reaction $A + B \longrightarrow C + D$ follows following rate law: rate = $k[A]^{1/2}[B]^{1/2}$. Stating with initial conc. of 1M of A and B each, what is the time taken for concentration of A to become 0.25 M.

Given: k = 2.303×10^{-3} sec^{-1}

(A) 300sec. (B) 600 sec.

(C) 900 sec. (D) 1200 sec.

Q.16 The reaction $A (g) \longrightarrow B(g) + 2C (g)$ is a first order reaction with rate constant $3.465 \times 10^{-6} s^{-1}$.Starting with 0.1 mole of A in 2 litre vessel, find the concentration of A after 200 sec, when the reaction is allowed to take place at constant pressure and temperature

(A) 0.05 M (B) 0.025 M

(C) 0.0125 M (D) None of these

Q.17 In respect of the equation

$k = A \exp(-E_a / RT)$, which one of the following statements is correct?

(A) R is Rydberg's constant

(B) k is equilibrium constant

(C) A is adsorption factor

(D) E_a is the energy of activation

Q.18 Rate of a reaction can be expressed by Arrhenius equation as $k = Ae^{-E/RT}$

In this equation, E represents

(A)The fraction of molecules with energy greater than the activation energy of the reaction

(B)The energy above which all the colliding molecules will react

(C)The energy below which colliding molecules will not react

(D)The total energy of the reacting molecules at a temperature. T

Q.19 The rate constant, the activation energy and the Arrhenius parameter (A) of a chemical reaction at 25°C are

$3.0 \times 10^{-4}\ s^{-1}$, 104.4 $kJmol^{-1}$ and

$6.0 \times 10^4\ S^{-1}$ respectively. The value of the rare constant at T → ∞

(A) $2.0 \times 10^{-18} s^{-1}$ (B) $6.0 \times 10^{14} s^{-1}$
(C) Infinity (D) $3.6 \times 10^{30} s^{-1}$

Q.20 A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C. The energy of activation of the reaction is

(A) 43.85kJ/mol (B) 55.14kJ/mol
(C) 11.97kJ/mol (D) 6.65kJ/mol

Q.21 For the first order reaction $A \longrightarrow B + C$, carried out at 27°C if $3.8 \times 10^{-16}\%$ of the reaction molecules exists in the activated state, the E_a(activation energy) of the reaction is [log 3.8 = 0.58]

(A) 12 kJ/mole (B) 831.4kJ/mole
(C) 100 kJ/mole (D)88.57kJ/mole

Q.22 In a reaction carried out at 400 K. 0.0001% of the total number of collisions are effective. The energy of activation of the reaction is

(A) zero (B) 7.37k cal/mol
(C) 9.212 k cal/mol (D) 11.05k cal/mol

Q.23 Select incorrect statement(s)

(A) Unit of pre-exponential factor (A) for second order reaction is mol L^{-1} s^{-1}
(B) A zero-order reaction must be a complex reaction
(C) Molecularity is defined only for RDS in a complex reaction
(D)Decay constant (λ) of radioactive substance is affected by temperature

Q.24 In a consecutive reaction system $A \xrightarrow{E_1} B \xrightarrow{E_2} C$ when E_1 is much greater than E_2, the yield of B increase with

(A) Increase in temperature
(B) Decreases in temperature
(C) Increase in initial concentration of A
(D) Decrease in initial concentration of A

Q.25 Which of the following is/are correct statement?

(A) Stoichiometry of a reaction tells about the order of the elementary reaction.
(B) For a zero-order reaction, rate and the rate constant are identical
(C) A zero-order reaction is controlled by factors other than concentration of reactants.
(D) A zero-order reaction is always elementary reaction

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
(C)Statement-1 is true, statement-2 is false.
(D) Statement- 1 is false, statement-2 is true

Q.26 Statement-1: The time of completion of reaction of type A → product (order < 1) may be determined.

Statement-2: Reactions with order ≥ 1 are either too slow or too fast and hence the time of completion cannot be determined

Q.27 Statement-1: A catalyst provides an alternative path to the reaction in which conversion of reaction into products takes place quickly

Statement-2: The catalyst forms an activated complex of lower potential energy with the reactants by which more number of molecules are able to cross the barrier per unit of time.

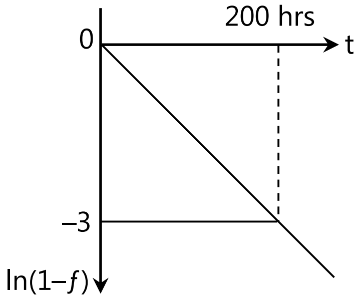
Paragraph 1

Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidised metal $(1 - f)$ surface thickness relative to maximum thickness (T) of oxidised surface, when metal surface is exposed to air for considerable period of time

Rate law: $\frac{df}{dt} = k(1 - f)$, where $f = x/T$,

x = thickness of oxide film at time 't'
& T = thickness of oxide film at t = ∞

A graph of $\ln(1 - f)$ vs t is shown a the adjacent figure



Q.28 The time taken for thickness to grow 50%of T is

(A) 23.1 hrs (B) 46.2hrs

(C) 100 hrs (D) 92.4 hrs

Q.29 The exponential variation of 'f' with t(hrs) is given by

(A) $[1 - e^{-3t/200}]$ (B) $e^{-3t/200} - 1$

(C) $e^{-3t/200}$ (D) $e^{3t/200}$

Paragraph 2

A reaction is said to be first order if it's rate is proportional to the concentration of reactant. Let us consider a reaction

$$A(g) \longrightarrow B(g) + C(g)$$

At t = 0 a 0 0

At time t a - x x x

The rate of reaction is oven by the expression $\frac{dx}{dt}$ =k(a – x) and integrated rate equation for a given

reaction is represented as $k = \frac{1}{t} \ln\left(\frac{a}{a-x}\right)$

where a = initial concentration and

(a – x) = concentration of A after time t.

Q.30 Thermal decomposition of compound X is a first order reaction If 75% of X is decomposed in 100 min. How long will it take for 90% of the compound to decompose? Given: log 2 = 0.30

(A) 190 min (B) 176.66 min

(C) 166.66 min (D) 156.66 min

Q.31 Consider a reaction $A(g) \longrightarrow 3B(g) + 2C(g)$ with rate constant 1.386×1^{-2} min^{-1}. Starting with 2 moles of A in 12.5 litre vessel initially, if reaction is allowed to takes place at constant pressure & at 298 K then find the concentration of B after 100 min.

(A) 0.04 M (B) 0.36 M

(C) 0.09 M (D) None of these

PREVIOUS YEARS' QUESTIONS JEE MAIN

Q.1 For a reaction $\frac{1}{2}A \rightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of B' by the expression **[2008]**

(A) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$ (B) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$

(C) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$ (D) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

Q.2 The rate of a chemical reaction doubles for every 10° C rise of temperature. If the temperature is raised by 50° C, the rate of the reaction increases by about **[2011]**

(A) 10 times (B) 24 times

(C) 32 times (D) 64 times

Q.3 In a first order reaction the concentration of reactant decreases from 800mol/dm^3 to 50 mol/dm^3 in 2×10^2 sec. The rate constant of reaction in sec^{-1} is **[2003]**

(A) 2×10^4 (B) 3.45×10^{-5}

(C) 1.386×10^{-2} (D) 2×10^{-4}

Q.4 Consider the reaction,
$2A + B \rightarrow$ Products
When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is **[2007]**

(A) L mol^{-1} s^{-1} (B) No unit

(C) mol L^{-1} s^{-1} (D) s^{-1}

Q.5 The rate constant for the reaction,
$2N_2O_5 \rightarrow 4NO_2 + O_2$ is 3×10^{-5} sec^{-1}. If the rate is 2.40×10^{-5}mol litre^{-1} sec^{-1}.
Then the concentration of N_2O_5
(in mol litre^{-1}) is **[2001]**

(A) 1.4 (B) 1.2 (C) 0.04 (D) 0

Q.6 The half-life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301) **[2009]**

(A) 230.3 minutes (B) 23.03 minutes

(C) 46.06 minutes (D) 460.6 minutes

Q.7 A reaction involving two different reactants **[2005]**

(A) Can never be a second order reaction

(B) Can never be a unimolecular reaction

(C) Can never be a bimolecular reaction

(D) Can never be a first order reaction

Q.8 A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will **[2006]**

(A) Remain unchanged (B) Triple

(C) Increase by a factor of 4 (D) Double

Q.9 For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A][B]^2$ then the order of the reaction is **[2002]**

(A) 3 (B) 6 (C) 5 (D) 7

Q.10 The following mechanism has been proposed for the reaction of NO with Br_2 to from NOBr: $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$

$NOBr_2(g) + NO(g) \rightarrow 2NOBr(g)$
If the second step is the rate determining step, the order of the reaction with respect to NO(g) is **[2006]**

(A) 1 (B) 0 (C) 3 (D) 2

Q.11 Consider the reaction
$Cl_{2(aq)} + H_2S_{(aq)} \rightarrow S_{(s)} + 2H^+_{(aq)} + 2Cl^-_{(aq)}$
The rate equation for this reaction is
rate = $k[Cl_2][H_2S]$
Which of these mechanisms is/are consistent with this rate equation
A. $Cl_2 + H_2S \rightarrow H^+ + Cl^- + Cl^- + HS^-$ (slow)
$Cl^+ + HS^- \rightarrow H^+ + Cl^- + S$ (fast)
B. $H_2S \rightleftharpoons H^+ + HS^-$ (fast equilibrium)

$Cl_2 + HS^- \rightarrow 2Cl^- + H^+ + S$ (slow) **[2010]**

(A) A only (B) B only

(C) Both A and B (D) Neither A nor B

Q.12 The time for half life period of a certain reaction $A \longrightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A' is 2.0 mol L^{-1}, how much time does it take for its concentration to come for 0.50 to 0.25 mol L^{-1} if it is a zero order reaction **[2010]**

(A) 1 h (B) 4h (C) 0.5h (D) 0.25 h

Q.13 The energies of activation for forward and reverse reactions for $A_2 + B_2 \longrightarrow 2AB$ are 180kJ mol^{-1} and 200kJ mol^{-1} respectively. The presence of catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \longrightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1}) **[2007]**

(A) 300 (B) 120 (C) 280 (D) 20

Q.14 Consider an endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions, respectively, in general **[2005]**

(A) $E_b < E_f$ (B) $E_b > E_f$ (C) $E_b = E_f$

(D) There is no definite relation between E_b and E_f

Q.15 If 'I' is the intensity of absorbed light and C is the concentration of AB for the photochemical process $AB + h\upsilon \rightarrow AB^*$, the rate of formation of AB* is directly proportional to **[2001]**

(A) C (B) I (C) I^2 (D) C.I

EXERCISE 1 JEE ADVANCED

Q.1 Ammonia and oxygen reacts at higher temperatures as

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

In an experiment, the concentration of NO increases by 1.08×10^{-2} mol litre^{-1} in 3 seconds. Calculate

(i) rate of reaction. (ii) rate of disappearance of ammonia (iii) rate of formation of water

Q.2 In the following reaction

$2H_2O_2 \longrightarrow 2H_2O + O$

rate of formation of O_2 is 3.6 M min^{-1}

(i) What is rate of formation of H_2O ?

(ii) What is rate of disappearance of H_2O_2?

Q.3 In a catalytic experiment involving the Haber process $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction was measured as

Rate = $\frac{\Delta[NH_3]}{\Delta t} = 2 \times 10^{-4}$ mol L^{-1} s^{-1}.

If there were no sides reactions, what was the rate of reaction expressed in terms of (a) N_2, (b) H_2?

Q.4 The reaction $2A + B + C \longrightarrow D + E$ is found to be first order in A second order in B and zero order in C. (1)

Give the rate law for the reaction in the form of differential equation.

(ii) What is the effect in rate of increasing concentrations of A, B, and C two times?

Q.5 At 27°C it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of reaction (in M sec^{-1}) and rate of reaction in term of pressure.

Q.6 For the elementary reaction $2A + B_2 \longrightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

Q.7 For the reaction $3BrO^- \longrightarrow BrO^-_3 + 2Br^-$ in an alkaline aqueous solution the value of the second order (in BrO^-) rate constant at 80°C in the rate law for $-\frac{\Delta[BrO^-]}{\Delta t}$ was found to be 0.056L mol^{-1} s^{-1}.

What is the rate of constant when the rate law is written for (a) $\frac{\Delta[BrO_3^-]}{\Delta t}$ (b) $\frac{\Delta[Br^-]}{\Delta t}$?

Q.8 Dinitropentoxide decomposes as follows:

$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

Given that $-d[N_2O_5]/dt = k_1[N_2O_5]$

$d[NO_2]/dt = k_2[N_2O_5]$; $d[O_2]/dt = k_3[N_2O5]$

What is the relation between k_1, k_2 and k_3?

Q.9 Suppose that the Sum consists entirely of hydrogen atom and releases the energy by the nuclear reaction.

$4\,{}^1_1H \longrightarrow {}^4_2He$ with 26 MeV of energy released. If the total output power of the Sun is assumed to remain constant at 3.9×10^{26} W find the time it will take to burn all the hydrogen. Take the mass of the Sum as 1.7×10^{30}kg.

Q.10 The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8$ atm. Calculate the ratio of rate of reaction relative to initial rate when P_C becomes 0.2 atm.

Q.11 In the following reaction, rate constant is 1.2×10^{-2} M s^{-1} $A \longrightarrow B$. What is concentration of B after 10 and 20 min, if we start with 10 M of A.

Q.12 For the following data for the zero order reaction $A \longrightarrow$ products. Calculate the value of k.

Time(min)	[A]
0.0	0.10 M
1.0	0.09 M
2.0	0.08 M

Q.13 The rate constant for a zero order reaction is 2×10^{-2} mol L^{-1} sec^{-1}, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.

Q.14 A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+, if the rate constant of disappearance of H^+ is

1×10^7 mole liter^{-1} sec^{-1}. How long would it take for H^+ in drop to disappear?

Q.15 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

Q.16 A first order reaction is 75% completed in 72min. How long time will it take for

(i) 50% completion (ii) 87.5% completion

Q.17 A first order reaction is 20% complete in 10 min. calculate (i) the specific rate constant. (ii) the time taken for the reactions to go to 75% completion.

Q.18 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place in ten times that required for half of the reaction.

Q.19 A first order reaction has a rate constant is 1.5×10^{-3} sec^{-1}. How long will 5.0 g of this reactant take to reduce to 1.25 g?

Q.20 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?

Q.21 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0% of the virus was found to be inactivated per minute. Evaluate k for inactivation process.

Q.22 If a reaction $A \longrightarrow$ Products, the concentrations of reactant A are C_0, aC_0, a^2C_0, a^3C_0 ....after time interval 0, t, 2t, 3t,........... where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also calculate the relation in k. a and t.

Q.23 The reaction

$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is a first order gas reaction with $k = 2.2 \times 10^{-5}$ sec^{-1} at 320°C. What % of SO_2Cl_2 is decomposed on heating this gas for 90 min?

Q.24 Two substances A($t_{1/2}$ = 5 mins) and B($t_{1/2}$ = 15 mins) follow first order kinetics are taken in such a way that initially [A]= 4 [B]. Calculate the time after which the concentration of both the substance will be equal.

Q.25 At 800° C the rate of reaction

$$2NO + H_2 \longrightarrow N_2 + H_2O$$

Changes with the concentration of NO and H_2 are

	[NO] in M	$[H_2]$ in M	$-\frac{1}{2}\frac{d[NO]}{dt}$ in M sec^{-1}
(i)	1.5×10^{-4}	4×10^{-3}	4.4×10^{-4}
(ii)	1.5×10^{-4}	2×10^{-3}	2.2×10^{-4}
(iii)	3.0×10^{-4}	2×10^{-3}	8.8×10^{-4}

(a) What is the order of this reaction?

(b) What is the rate equation for the reaction?

(c) What is the rate when

$[H_2] = 1.5 \times 1^{-3}$ M and [NO] $= 1.1 \times 1^{-3}$M?

Q.26 The data below are for the reaction if NO and Cl_2 to form NOCl at 295 K

Concentration of Cl_2 [M]	Concentration of NO	Initial Rate (M s^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order w. r.t. NO and Cl_2 in the reaction.

(b) Write the rate expression

(c) Calculate the rate constant

(d) Determine the reaction rate when concentration of Cl_2 and NO are 0.2 M & 0.4 M respectively.

Q.27 The catalytic decomposition of N_2O by gold at 900 °C and at an initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes

(i) What is the order of the reaction?

(ii) Calculate the velocity constant

(iii) How much of H_2O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

Q.28 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below

t (sec)	0	100	200	300
Pa(Pascal)	4×10^3	3.5×10^3	3×10^3	2.5×10^3

Determine the order of reaction, its rate constant.

Q.29 The half -life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Q.30 In this case we have

$A \longrightarrow B + C$

Time	t	∞
Total pressure of A + B +C	P_2	P_3

Find k.

Q.31 $A \longrightarrow B + C$

Time	t	∞
Total pressure of (B +C)	P_2	P_3

Find k.

Q.32 $A \longrightarrow B + C$

Time	0	t
Volume of reagent	V_1	V_2

The reagent reacts with A, B and C. Find k. [Assuming n-factor of A B & C are same]

Q.33 $A \longrightarrow 2B + 3C$

Time	t	∞
Volume of reagent	V_2	V_3

The reagent reacts with A, B and C.

Find k. [Assuming n-factor of A B & C are same]

Q.34 $S \longrightarrow G + F$

Time	t	∞
Rotation of Glucose & Fructose	r_1	r_∞

Find k.

Q.35 The reaction $AsH_3(g) \longrightarrow As(s) + \frac{3}{2} H_2(g)$ was followed at constant volume at 310°C by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.

Time (in hrs)	0	5	7.5	10
Total pressure (in min)	758	827	856	882

Q.36 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction.

$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$

at 500°C is as follow:

Time (sec.)	390	1195	3155	∞
Pressure increase (mm Hg)	96	250	467	619

The initial pressure of ether was 312 mm Hg. Write the rate equation for this reaction and determine the rate constant of reaction

Q.37 From the following data show that decomposition of H_2O_2 in aqueous is first order.

Time in (minutes)	0	10	20
Volume (in c.c. of $KMnO_4$)	22.8	13.3	8.25

Q.38 The following data were obtained in experiment on inversion of cane sugar

Time (minute	0	60	120	1805	360	∞
Angle of rotation (degree)	+13.1	+11.6	+10.2	+9.0	+5.87	−3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

Q.39 At 100°C the gaseous reaction $A \longrightarrow 2B + C$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half-life period of the reaction?

Q.40 The decomposition of N_2O_5 according to the equation

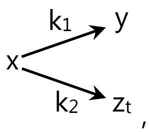
$2N_2O_5\ (g) \longrightarrow 4\ NO_2(g) + O_2(g)$ is a first order reaction. After 30 min, from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction

Q.41 A definite volume of H_2O_2 undergoing spontaneous decomposition required 22.8 c.c. of standard permanganate solution for titration. After 10 and 20 minutes respectively the volumes of permanganate required were 13.8 and 8.25 c.c.
(a) Find order of reaction. How may the result be explained?
(b) Calculate the time required for the decomposition to be half completed.
(c) Calculate the fraction of H_2O_2 decomposed after 25 minutes.

Q.42 Hydrogen peroxide solution was stored in a mild steel vessel. It was found, however, that the hydrogen peroxide decomposed on the wall of the vessel (a first order reaction) An experiment with 100 ml of a solution gave 10.31 ml oxygen (corrected to 1 atm & 273 K) after 5.1 days. Find how long the peroxide can be stored before the loss of 20.00 ml oxygen occurs (per 100 ml solution) under similar storage conditions if complete decomposition of the sample to H_2O_2 gave 46.34 ml oxygen.

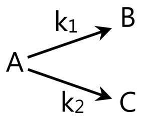
Q.43 The reaction $A(aq) \longrightarrow B\ (aq) + C\ (aq)$ is monitored by measuring optical rotation of reaction mixture as different time interval The species A. B and C are optically active with specific rotations 20°, 30° and – 40° respectively. Starting with pure A if the value of optical rotation was found to be 2.5° after 6.93 minutes and optical rotation was –5° after infinite time. Find the rate constant for first order conversion of A into B and C.

Q.44 For a reaction



Calculate value of ratio, $\frac{[x]_t}{[y]+[z]}$ at any given instant

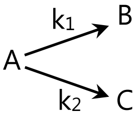
Q.45



$k_1 = x\ hr^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\frac{[C]}{[A]}$ after one hour from the start of the reaction. Assuming only A was present in the beginning.

Q.46 How much time would be required for the B to reach maximum concentration for the reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C.$
Given $k_1 = \frac{\ln 2}{4}$ $k_2 = \frac{\ln 2}{2}$

Q.47 For first order parallel reaction k_1 and k_2 are 8 and 2 min^{-1} respectively at 300 K. If the activation energies for the formation of B and C are respectively 20 and 28.314 kJ/ mol respectively find the temperature at which B and C will be obtained in molar ratio of 2:1.



[Given: ln4 = 1.4]

Q.48 In gaseous reactions important for understanding the upper atmosphere, H_2 O and O react bimolecularly to form two OH radicals ΔH for This reaction is 72 kJ at 500 K and E_a = 77 kJ mol^{-1}, then calculate E_a for the biolecular recombination of 2OH radicals to form H_2O & O at 500 K.

Q.49 The energy of activation of a first order reaction is 104.5 kJ $mole^{-1}$ and pre - exponential factor (A) is 5 × 10^11 sec^{-1}. At what temperature, will the reaction have a half-life of 1 minute?

Q.50 the specific rate constant for a reaction increases by a factor of 4. If the temperature is changed from 27°C to 47°C. Find the activation energy for the reaction

Q.51 The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/ mole and 3.46×10^{-3} sec^{-1} respectively. Determine the temperature at which half life of the reaction is 2 hours.

Q.52 A catalyst lowers the activation energy for a certain reaction from 75 kJ to

25 kJ mol^{-1}. What will be the effect on the rate of reaction at 25°C after things being equal?

Q.53 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate.

Q.54 At 380°C the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C.

Q.55 The reaction $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism

(i) $NO + Br_2 \xrightleftharpoons{\text{fast}} NOBr_2$

(ii) $NOBr_2 + NO \xrightarrow{\text{slow}} 2NOBr$

Suggest the rate law expression.

Q.56 For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested

$2NO \longrightarrow N_2O_2$ equilibrium constant K_1 (fast)

$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ (slow)

$N_2O + H_2 \xrightarrow{k_3} H_2 + H_2O$ (fast)

Establish the rate law for given reaction.

Q.57 Reaction between NO and O_2 to form NO_2 is $2NO + O_2 \longrightarrow 2NO_2$ follows the following mechanism

$NO + NO \xrightleftharpoons[k-1]{K_1} N_2O_2$ (in rapid equilibrium)

$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (stow)

Show that the rate of reaction is given by

$$\frac{1}{2}\left(\frac{d[NO_2]}{dt}\right) = K[NO]^2[O_2]$$

Q.58 Deduce rate law expressions for the conversion of H_2 and I_2 to HI at 400°C corresponding to each of the following mechanisms:

(a) $H_2 + I_2 \longrightarrow 2HI$ (one step)

(b) $I_2 \longrightarrow 2I$

$2I + H_2 \longrightarrow 2HI$ (slow)

(c) $I_2 \longrightarrow 2I$

$I + H_2 \longrightarrow IH_2$

$IH_2 + I \longrightarrow 2HI$ (slow)

(d) Can the observed rate law expression rate $= k[H_2][I_2]$ distinguish among these mechanisms?

(e) If it is known that ultraviolet light causes the reaction of H_2 and I_2 to proceed at 200°C with the same rate law expression, which of these mechanisms becomes most improbable?

EXERCISE 2 JEE ADVANCED

Q.1 The rate of a reaction is expressed in different ways as follows:

$$+\frac{1}{2}\left(\frac{d[C]}{dt}\right)=-\frac{1}{3}\left(\frac{d[D]}{dt}\right)=+\frac{1}{4}\left(\frac{d[A]}{dt}\right)=-\left(\frac{d[B]}{dt}\right)$$

The reaction is:

(A) $4A + B \longrightarrow 2C + 3D$

(B) $B + 3D \longrightarrow 4A + 2C$

(C) $A + B \longrightarrow C + D$

(D) $B + D \longrightarrow A + C$

Q.2 For the reaction system $2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2(g)$ volume is suddenly reduced to half of its value by increasing the pressure on it. If the reaction is first order with respect to O_2 and second order with respect to NO the rate reaction will

(A) Increase to four times of its initial value

(B) Diminish to one-fourth of its initial value

(C) Diminish to one-eight of its initial value

(D) Increase to eight times of its initial value

Q.3 The energies of activation for forward and reverse reactions for

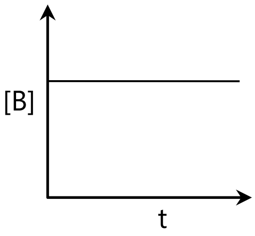
$A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1}

and 200 $kJmol^{-1}$ respectively. The presence of catalyst lower the activation energy of both(forward and reverse) reactions by 100 kJ mol^{-1}. The magnitude of enthalpy change of the reaction ($A2 + B_2 \longrightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1}).

(A) 300 (B) 120 (C) 20 (D) –20

Q.4 Which graph represents zero order reaction [A(g) $\longrightarrow$ B(g)]

(A)



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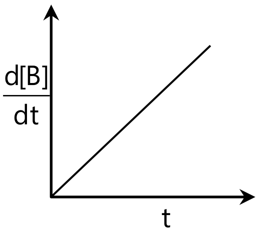

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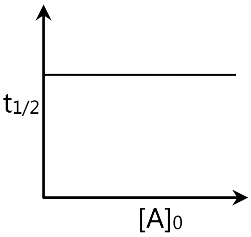

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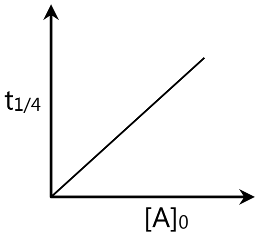
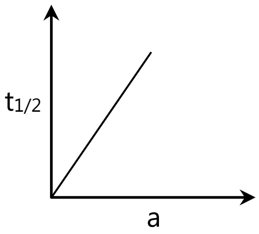
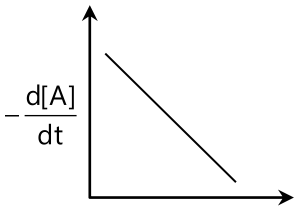


Q.5 Consider the reaction A → B, graph between half-life($t_{1/2}$) and initial concentration (a) of the reaction is



Hence graph between $-\frac{d[A]}{dt}$ and time will be

(A)



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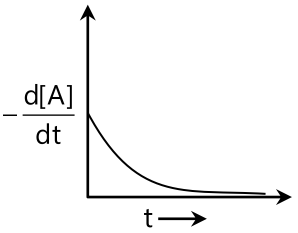
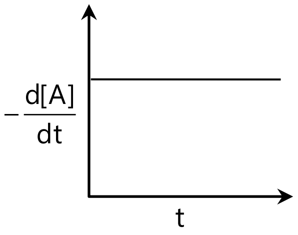
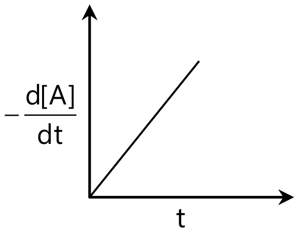


(C)



(D)



Q.6 The reactions of higher order are rare because

(A) Many body collisions involve very high activation energy

(B) Many body collisions have a very low probability

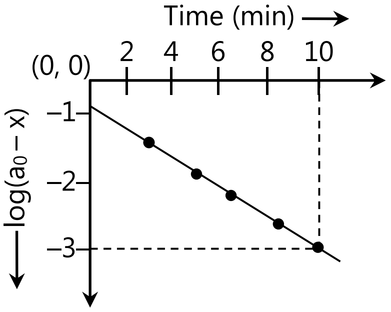
(C)Many body collisions are not energetically favoured

(D) Many body collisions can take place only in the gaseous phase.

Q.7 For the first order decomposition of $SO_2Cl_2(g)$.

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

a graph of log (a_0 – x) vs t is shown in figure. What is the rate constant (sec^{-1})?



(A) 0.2 (B) 4.6×10^{-1}

(C) 7.7×10^{-3} (D) 1.15×10^{-2}

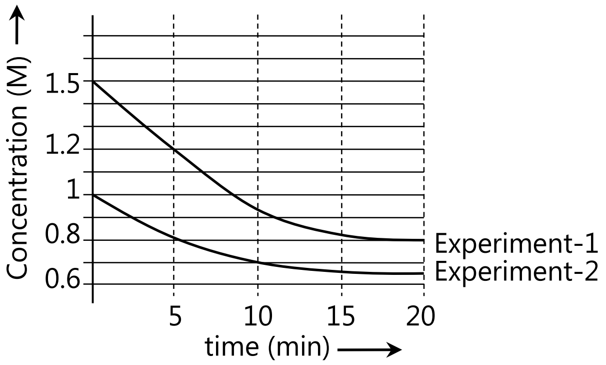
Q.8 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as "16.8 V" was left open Due to this, some H_2O_2 decomposed. To determine the new volume strength after 2.303 hours. 20 mL of this solution was diluted to 100 mL 25 mL of this diluted solution was titrated against 37.5 mL of 0.02 M $KMnO_4$ solution under acidic conditions [Given: STP is 1 atm and 273 K]

The rate constant (in hr^{-1}) for decomposition of H_2O_2 is:

(A) 0.15 (B) 0.30 (C) 0.60 (D) 1.3

Q.9 The variation of concentration of A with time in two experiments starting with two different initial concentration of A is given in the following graph. The reaction is represented as A (aq) ⟶ B(aq).

What is the rate of reaction (M/min) when concentration of A in aqueous solution was 1.8 M?



(A) 0.08 M min^{-1} (B) 0.036 M min^{-1}

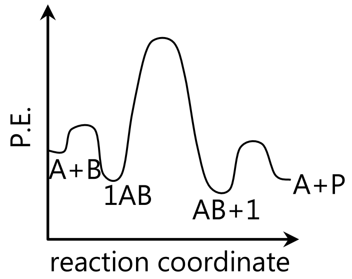
(C) 0.13 M min^{-1} (D) 1 M min^{-1}

Q.10 The following mechanism has been proposed for the exothermic catalyzed complex reaction.

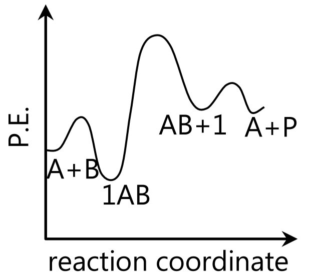
$A+B \overset{fast}{\rightleftharpoons} IAB \xrightarrow{k_1} AB+I \xrightarrow{k_2} P+A$

If k_1 is much smaller than k_2. The most suitable qualitative plot of potential energy (PE.) versus reaction coordinate for the above reaction.

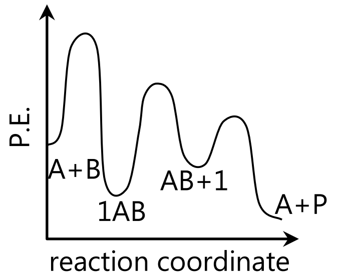
(A)



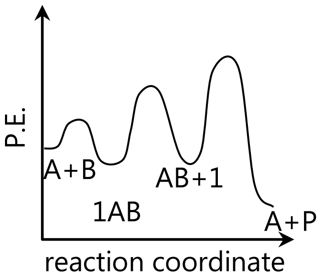
(B)



(C)



(D)



Q.11 The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr

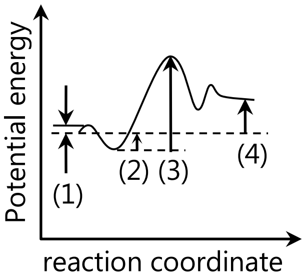
$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$$

$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is

(A) 2 (B) 1 (C) 0 (D) 3

Q.12 Choose the correct set of indentifications.



	(1)	(2)	(3)	(4)
(A)	ΔE for E+S→ES	E_a for ES→EP	$\Delta E_{overall}$ for S→P	E_a for EP→E+P
(B)	E_a for E+S→ES	ΔE for E+S→ES	E_a for ES→EP	$\Delta E_{overall}$ for S→P
(C)	E_a for ES→EP	E_a for EP→E+P	$\Delta E_{overall}$ for S→P	ΔE for EP→E+P
(D)	E_a for E+S→ES	E_a for ES→EP	E_a for EP→E+P	$\Delta E_{overall}$ for S→P
(E)	ΔE for E+S→ES	$\Delta E_{overall}$ for S→P	ΔE for EP→E+P	$E_a$for EP→E+P

Q.13 SO_3 gas is entering the environment at a constant rate of 6.93×10^{-5} gm/L/day due to the emission of polluting gases from thermal power plant but at the same time it is decomposing & following first order kinetics with half life of 100 days.

Based on above information select the true statement (s).

(A) Concentration of SO_3 in Kota is 1.25×10^{-5} M (Assume SO_3 present in air reaches steady state)

(B) If 10^3 L of air is passed through 1L pure water (assuming all SO_3 to be dissolved in it) & resulting solution is titrated against 1 N NaOH solution, 15 ml is required to reach end point

(C) An industry is manufacturing H_2SO_4 at the rate of 980 kg per day with the use of SO_3 in air it should use 8×10^5 litre air/day

(D) If SO_3 emission is stopped then after 1000 days its concentrations will reduce to $\approx 1.2 \times 1^{-3}$ M.

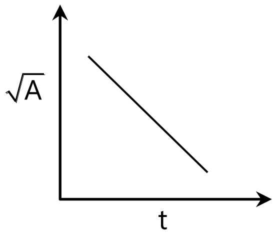
Q.14 For the reaction A $\longrightarrow$ B. the rate law expression is $-\frac{d[A]}{dt} = k[A]^{1/2}$. If initial concentration of [A] is $[A]_0$, then

(A) The integrated rate expression is $k = \frac{2}{t}(A_0^{1/2} - A^{1/2})$

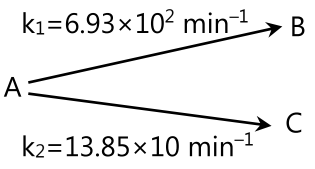
(B) The graph of $\sqrt{A}$ Vs t will be

(C) The half-life period $t_{1/2} = \frac{K}{2[A]_0^{1/2}}$

(D)The time taken for 75% completion of reaction $t_{3/4} = \frac{\sqrt{[A]_0}}{k}$



Q.15 Consider the reaction,


$k_1 = 6.93 \times 10^2$ min^{-1}
B
A
C
$k_2 = 13.85 \times 10$ min^{-1}

A, B and C all are optically acme compound. If optical rotation per unit concentration of A, B and C are 60°, –72°, 42° and initial concentration of A is 2 M then select write statements(s).

(A) Solution will be optically active and dextro after very long time

(B) Solution will be optically active and laevo after very long time

(C) Half life of reaction is 15 min

(D) After 75% conversion of A in to B and C angle of rotation of solution will be 36°

Q.16 Which of the following statement is incorrect?

(A)The order of reaction is the sum of powers of all the concentration terms in the rate equation.

(B) The order of reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentrations of all other react ants constant.

(C)Orders of reactions cannot be fractional

(D)The order of a reaction can only be determined from the stoichiometric equation for the reaction

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1

(B) Statement–1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement–1 is true, statement-2 is false.

(D) Statement–1 is false, statement-2 is true.

Q.17 Statement-1: A fractional order reaction must be a complex reaction.

Statement-2: Fractional order of RDS equals to overall order of a complex reaction.

Q.18 Statement–1: Temperature coefficient of a one step reaction may be negative

Statement–2: The rate of reaction having negative order with respect to a reactant decreases with the increase m concentration of the reactant

Q.19 Statement–1: The overall rate of a reversible reaction may decrease with the increase in temperature.

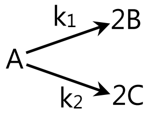
Statement–2 : When the activation energy of forward reaction is less than that of backward reaction, then the increase in the rate of backward reaction is more than that of forward reaction on increasing the temperature

Q.20 Statement–1: In a reversible endothermic reaction E of forward reaction is higher than that of backward reaction

Statement–2: The threshold energy of forward reaction is more than that of backward reaction

Paragraph-1:

For a hypothetical elementary reaction



where $\frac{k_1}{k_2} = \frac{1}{2}$ Initial only 2 moles of A are present.

Q.21 The total number of moles of A, B & C at the end of 50% reaction are

(A) 2 (B) 3 (C) 4 (D) 5

Q.22 Number of moles of B are

(A) 2 (B) 1 (C) 0.666 (D) 0.33

Paragraph-2:

The gaseous reaction: $n_1 A(g) \longrightarrow n_2B\ (g)$ is first order with respect to A. The true race constant of reaction is k. The reaction is studied at a constant pressure and temperature. Initially, the moles of A were 'a' and no B were present.

Q.23 How many moles of A are present at time, t?

(A) $a \cdot e^{-kt}$ (B) $a \cdot e^{-n_1kt}$

(C) $a \cdot e^{-n_2kt}$ (D) $a(1-e^{-n_2kt})$

Q.24 If the initial volume of system were v_{0° then the volume of system after time, t, will be

(A) $\frac{n_1v_0}{n_2}$ (B) $\frac{n_2v_0}{n_1}$

(C) $v_0\left[\frac{n_2}{n_1}+\left(1-\frac{n_2}{n_1}\right)\cdot e^{-n_1kt}\right]$

(D) $v_0\left[\frac{n_2}{n_1}+\left(\frac{n_2}{n_1}-1\right)\cdot e^{-n_2kt}\right]$

Q.25 What will be the concentration of A at time t, if $n_1 = 1$ and $n_2 = 2$?

(A) $[A_0]\ .e^{-kt}$ (B) $[A_0]\left(\frac{e^{-kt}}{2-e^{-kt}}\right)$

(C) $[A_0]\left(\frac{e^{-kt}}{1-e^{-kt}}\right)$ (D) $[A_0](1-2\ .\ e^{-kt})$

Paragraph-3:

For the reaction sequential reaction

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

the concentration of A, B & C at anytime 't' is given by

$[A]_1 = [A]_0e^{-kt}$; $[B]_1 = \frac{k_1[A]_0}{(k_2-k_1)}[e^{-k_1t} - e^{-k_2t}]$

$[C]_1 = [A_0] - ([A]_1 + [B]_1)$

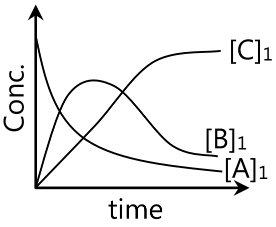
Q.26 The time at which concentration of B is maximum is

(A) $\frac{k_1}{k_2-k_1}$ (B) $\frac{1}{k_2-k_1}\ln\frac{k_1}{k_2}$

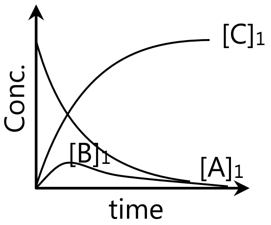
(C) $\frac{1}{k_1-k_2}\ln\frac{k_1}{k_2}$ (D) $\frac{k_2}{k_2-k_1}$

Q.27 Select the correct option if $k_1 = 1000s^{-1}$ and $k_2 = 20s^{-1}$.

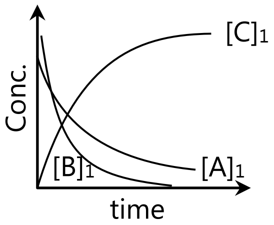
(A)



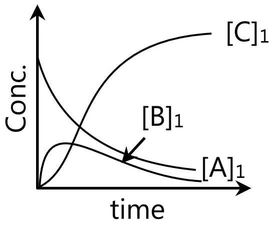
(B)



(C)



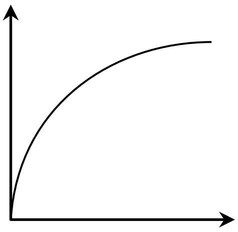
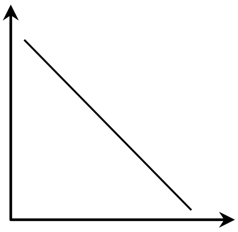
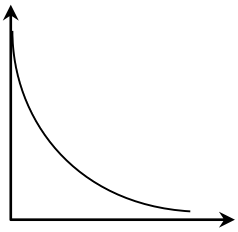
(D)

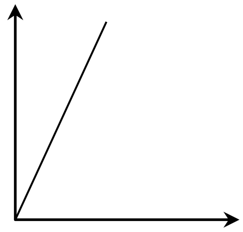


Match the Column:

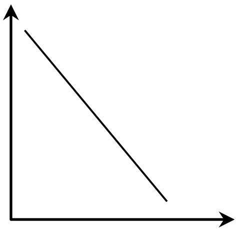
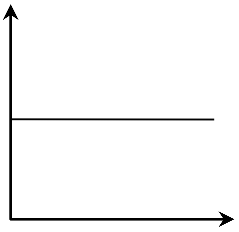
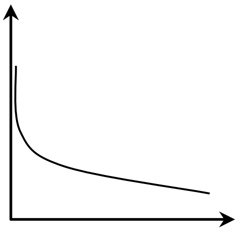
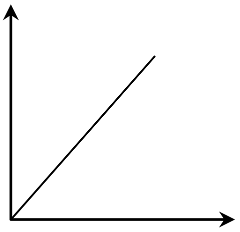
Q.28 For the reaction of type $A(g) \longrightarrow 2B(g)$

Column – I contains four entries and **Column – II** contains four entries. Entry of column –I are to be matched with only one entry of column-II

Column-I		**Column-II**	
(A)	$\frac{d[B]}{dt}$ vs $\frac{-d[A]}{dt}$ for first order	(P)	
(B)	[A] vs t for first order	(Q)	
(C)	[B] vs t for first order	(R)	

(D)	[A] vs t for zero order	(S)	

Q.29 Column-I and **Column-II**. Entry of **Column-I** are to be matched with one or more than one entries of **Column-II** and vice versa.

	Column-I (Graphs reaction A → Products)		**Column-II (Co-ordinates)**
(A)		(P)	In [A] (y-axis), t(x-axis)(order = 1)
(B)		(Q)	$t_{1/2}$(y-axis), [A_0] (x-axis) (order = 1)
(C)		(R)	r(y-axis), t(x-axis)(order > 0)
(D)		(S)	r(y-axis), t(x-axis)(order = 0)
		(T)	$t_{1/2}$(y-axis), [A_0] (x-axis) (order > 1)
		(U)	$\frac{1}{[A]}$ (y-axis), t(x-axis)(order = 2)
		(V)	r(y-axis), [A](x-axis)(order = 1)

PREVIOUS YEARS' QUESTIONS JEE ADVANCED

Q.1 The rate constant of a reaction depends on **(1981)**

(A) Temperature
(B) Initial concentration of the reactants
(C) Time of reaction
(D) Extent of reaction

Q.2 A catalyst is a substance which **(1983)**

(A) Increases the equilibrium concentration of the product
(B) Changes the equilibrium constant of the reaction
(C) Shortens the time to reach equilibrium
(D) Supplies energy to the reaction

Q.3 If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process.

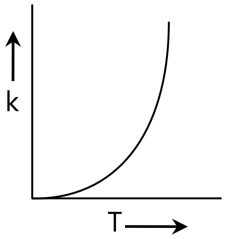
AB + hv → AB*, the rate of formation of AB* is directly proportional to **(2001)**

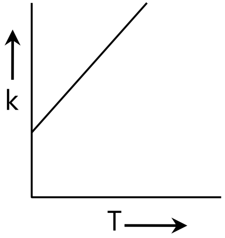
(A) C (B) I (C) I^2 (D) C.I

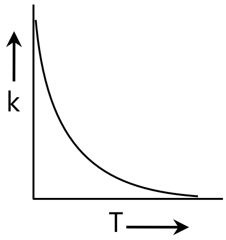
Q.4 Which one of the following statements is incorrect about order of reaction? **(2005)**

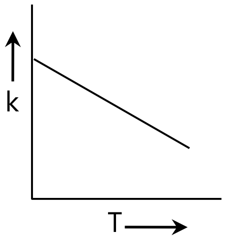
(A) Order of reaction is determined experimentally
(B) Order of reaction is equal to sum of the power of concentration terms in differential rate law
(C) It is not affected with stoichiometric coefficient of the reactants
(D) Order cannot be fractional

Q.5 Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is **(2010)**

(A)


(B)


(C)


(D)


Comprehension (Q.6), (Q. 7), (Q.8)

Carbon-14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.

$$^{14}_{7}N + {}_0n^1 \longrightarrow {}^{14}_{6}C + {}_1p^1$$

^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C–14 undergoes

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + \beta^-$$

The half-life period of ^{14}C is 5770 yr.

The decay constant (λ) can be calculated by using the following formula

$$\lambda = \frac{0.693}{t_{1/2}}$$

The comparison of the β^- activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 yr. The proportion of ^{14}C to ^{12}C in living matter is 1: 10^{12}. **(2006)**

Q.6 Which of the following option is correct?

(A) In living organisms, circulation of ^{14}C from atmosphere is high so the carbon content is constant in organism
(B) Carbon dating can be used to find out the age of earth crust and rocks
(C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbons content remains constant in living organisms
(D) Carbon dating cannot be used to determine concentration of ^{14}C in dead beings.

Q.7 What should be the age of fossil for meaningful determination of its age?

(A) 6 yr (B) 6000 yr

(C) 60,000 yr

(D) It can be used to calculate any age

Q.8 A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then

(A) the age of fossil will increase at the place where explosion has taken place and

$T_1 - T_2 = \frac{1}{\lambda}\ln\frac{C_1}{C_2}$

(B) the age of fossil will decrease at the place where explosion has taken place and

$T_1 - T_2 = \frac{1}{\lambda}\ln\frac{C_1}{C_2}$

(C) the age of fossil will be determined to be the same

(D) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$

Q.9 The concentration of R in the reaction $R \longrightarrow P$ was measured as a function of time and the following data obtained:

[R] (molar)	1.0	0.75	0.40	0.10
t (min)	0.0	0.05	0.12	0.18

The order of the reaction is **(2010)**

Q.10 Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 yr. What is the rate constant (in yr^{-1}) for the decay? What fraction would remain after 11540 yr?

(1984)

Q.11 A first order gas reaction has $A' = 1.5 \times 10^{-6}$ per second at 200° C If the reaction is allowed to run for 10 h, what percentage of the initial concentration would have change in the product? What is the half-life of this reaction?

(1987)

Q.12 An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life period of $_{42}Mo^{99}$ which is a beta emitter is 66.6 h. find the minimum amount of $_{42}Mo^{99}$ required to carry out the experiment in 6.909 h. **(1989)**

Q.13 The gas phase decomposition of dimethyl ether follows first order kinetics

$CH_3{-}O{-}CH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$

The reaction is carried out in a constant volume container at 500°C and has a half-life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal gas behaviour. **(1993)**

Q.14 (a)The rate constant of a reaction is $1.5 \times 10^7\ s^{-1}$ at 50° C and $4.5 \times 10^7\ s^{-1}$ at 100°C Evaluate the Arrhenius parameters A and E_a. **(1998)**

(b) For the reaction,

$N_2O_5\ (g) \longrightarrow 2NO_2\ (g) + \frac{1}{2} O_2\ (g)$

calculate the mole fraction $N_2O_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. . Assume ideal gas behaviour.

Q.15 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

Time (in min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

(A) Order of reaction

(B) Rate constant

(C)Time taken for 75% completion of reaction.

(D) Total pressure when p_x = 700 mm **(2005)**

• PlancEssential Questions •

RECOMMENDED DURING REVISION

EXERCISE 1 JEE MAIN/BOARDS

Q.1 Q.4 Q.7 Q.9 Q.12 Q.19
Q.24

EXERCISE 2 JEE MAIN

Q.2 Q.10 Q.16 Q.28 Q.29

PREVIOUS YEARS' QUESTIONS JEE MAIN

Q.9 Q.14 Q.15

EXERCISE 1 JEE ADVANCED

Q.7 Q.9 Q.20 Q.36 Q.43 Q.58(e)

EXERCISE 2 JEE ADVANCED

Q.8 Q.12 Q.23 Q.24 Q.28

PREVIOUS YEARS' QUESTIONS JEE ADVANCED

Q.12 Q.15

ANSWER KEY

EXERCISE 1 JEE MAIN/BOARDS

Q.1. (a) 6.25 ; (b) 14.3; (c) 0 %
Q.2. 2×10^{-2} min^{-1}
Q.3. P_1 = 379.55 mmHg, $t^{7/n}$ = 399.96 min
Q.4. 0.0207 min^{-1}
Q.5. k = 0.022 hr^{-1}
Q.6. 15.13 week
Q.7. 20 min
Q.8. 0.26: 1
Q.9. (a) 43.46 kJ mol^{-1} (b) 20.47 hour
Q.10. % decomposition = 67.21 %
Q.11. k = 0 0327 min^{-1}
Q.12. 0.537
Q.13. 4.83 mins
Q.14. 0 0025 m
Q.15. E_r=6 × 10^4 J; E_b = 9.3 × 10^4 J
Q.16. a = b= 1
Q.18. (a) $\frac{d(D)}{dt} = \frac{k_1k_3(A)(B)}{k_2+k_3}$
(b) $E_a = E_{a1} + E_{a3} - E_{a2}$ $A = \frac{A_1A_3}{A_2}$
Q.20. 0.0805
Q.21. 161 minutes
Q.22. 55.33 kJ mole^{-1}
Q.23. rate = K(A)[13]^2 rate will became 8 times
Q.24. K_{27} = 3.85 × 10^{-4} sec^{-1}
K_{47} = 11.55 × 10^{-4} sec^{-1}.
E = 43.78 kJ/mol
Q.25. It is first order kinetics with
k = 8.64 × 10^{-1}
Q.26. 2
Q.27. Ea = 2.2 × 10^4
A = 5.42 × 10^{10}
Q.28. (a) = 1 × 10^{-2} mol l^{-1} s^{-1}
(b) = 5.495 × 10^{-3} mol^{-1} l^{-1} s^{-1}
Q.29. Rate = 2 × 10^{-4} mol dm^{-3} min^{-1} x = 18.12%
Q.30. k = 0.02231 min^{-1} t = 62.07 min

EXERCISE 2 JEE MAIN/BOARDS

Q.1 B Q.2 A Q.3 A Q.4 D Q.5 D Q.6 D
Q.7 C Q.8 B Q.9 C Q.10 D Q.11 D Q.12 C
Q.13 C Q.14 D Q.15 B Q.16 A Q.17 D Q.18 C
Q.19 B Q.20 B Q.21 C Q.22 D Q.23 A, C, D Q.24 A,C
Q.25 A, B, C Q.26 C Q.27 A Q.28 B Q.29 A Q.30 C
Q.31 B

PREVIOUS YEAR QUESTIONS JEE MAIN

Q.1 A Q.2 C Q.3 C Q.4 A Q.5 D Q.6 C
Q.7 B Q.8 C Q.9 A Q.10 D Q.11 A Q.12 D
Q.13 D Q.14 A Q.15 B

EXERCISE 1 JEE ADVANCED

Q.1. (i) r= $\frac{1}{4}\frac{d[NO]}{dt}$ = 9 × 10^{-4} mol litre^{-1} sec^{-1}
(ii) 36 × 10^{-4} mol litre^{-1} sec^{-1}
(iii) 54 × 10^{-4} mol litre^{-1} sec^{-1}
Q.2. (i) 7.2 mol litre^{-1} min^{-1},
(ii) 7.2 mol litre^{-1} min^{-1}
Q.3. (a) 1 × 10^{-4} mol L^{-1} s^{-1},
(b) 3 × 10^{-4} mol L^{-1} s^{-1}
Q.4. (i) $\frac{dx}{dt}$ = k [A][B]^2
(ii) Rate increases by 8 times
Q.5. 8.12 × 10^{-6} Ms^{-1}, 0.012 atm min^{-1}
Q.6. Rate increases by 27 times
Q.7. (a) 0.019 mol L^{-1} s^{-1},
(b) 0.037 mol L^{-1} s^{-1}
Q.8. $2k_1 = k_2 = 4k_3$
Q.9. 2.72 × 10^{18} sec
Q.10. 1/6
Q.11. (i) 7.2 M, (ii) 10 M
Q.12. K= 0.01 M min^{-1}
Q.13. 0.75 M
Q.14. 6 × 10^{-9} sec
Q.15. 1.2 hr
Q.16. (i) 36 min (ii) 108 min
Q.17. (i) 0.0223 min^{-1}, (ii) 62.17 min
Q.19. 924.362 sec

Q.20. Expiry time = 41 months

Q.21. 3.3×10^{-4} s^{-1}

Q.22. $k = \frac{2.303}{t}\log\frac{1}{a}$

Q.23. 11.2%

Q.24. 15 min

Q.25. (a) Third order, (b) $r = k[NO]^2[H_2]$,
(c) 8.85×10^{-3} M sec^{-1}

Q.26. (a) Order w.r.t. NO = 2 and
w.r.t. Cl_2 = 1,
(b) $r = K[NO]^2[Cl_2]$,
(c) $K = 8$ L^2 mol^{-2}s^{-1},
(d) Rate = 0.256 mole L^{-1} s^{-1}

Q.27. (i) First order
(ii) $k = 1.308 \times 10^{-2}$ min^{-1}
(iii) 73%

Q.28. (i) Zero order, (ii) K = 5 Pa/s

Q.29. Zero order

Q.30. $k = \frac{1}{t}\ln\frac{P_3}{2(P_3 - P_2)}$

Q.31. $k = \frac{1}{t}\ln\frac{P_3}{(P_3 - P_2)}$

Q.32. $k = \frac{1}{t}\ln\frac{V_1}{(2V_1 - V_2)}$

Q.33. $k = \frac{1}{t}\ln\frac{4V_3}{5(V_3 - V_2)}$

Q.34. $k = \frac{1}{t}\ln\frac{r_\infty}{(r_\infty - r_1)}$

Q.35. First order

Q.36. (i) $r = K[(CH_3)_2O]_2$ 0.000428 sec^{-1}

Q.37. First order

Q.38. 966 min

Q.39. (a) 90 mm,
(b) 47 mm,
(c) 6.49×10^{-2} per minutes,
(d) 10.677 min.

Q.40. $k_1 = 2.605 \times 10^{-3}$ min^{-1}

Q.41. (a) first order,
(b) 13.75 minutes,
(c) 0.716 0.180 atm, 47.69 sec

Q.42. 11.45 days

Q.43. 0.1 min^{-1}

Q.44. $\frac{1}{e^{(K_1+K_2)}t - 1}$

Q.45. $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x} - 1)$

Q.46. t = 4 min

Q.47. 0379.75 K

Q.48. 5 kJ mol^{-1}

Q.49. 349.1 K

Q.50. 55.33 kJ mole^{-1}

Q.51. 306 K

Q.52. Rate of reaction increases
5.81×10^8 times

Q.53. 10.757 k cal mol^{-1}

Q.54. t=20.4 minutes 56. 2000 K

Q.55. $r = K'\,[NO]^2\,[Br_2]$

Q.56. $k = k_2'$

Q.57. $r = K[NO]^2\,[H_2]$, where $K = k_2 \times K_1/k^{-1}$

Q.58. (d) No, (e) mechanism (a) is incorrect

EXERCISE 2 JEE ADVANCED

Q.1 B **Q.2** D **Q.3** C **Q.4** D **Q.5** C **Q.6** B
Q.7 C **Q.8** C **Q.9** A **Q.10** A **Q.11** A **Q.12** B
Q.13 A, D **Q.14** A,B,D **Q.15** A, D **Q.16** C, D **Q.17** C **Q.18** D
Q.19 A **Q.20** C **Q.21** B **Q.22** C **Q.23** B **Q.24** D
Q.25 B **Q.26** C **Q.27** C
Q.28 A-S, B-R, C-P, D-Q **Q.29** A-P, B-Q, S C-R,T, D-V

PREVIOUS YEARS' QUESTIONS JEE ADVANCED

Q.1 A **Q.2** C **Q.3** D **Q.4** D **Q.5** A **Q.6** A
Q.7 B **Q.8** A **Q.9** 0 **Q.10** 0.25 **Q.11** 128.33h
Q.12 3.56x10^{-16} **Q.13** 0.75 atm **Q.14** 4.15x10^3 s^{-1}, 0.375
Q.15 **(a)** 1 **(b)** 693x10-3 min^{-1} **(c)** 200 min **(d)** 950 mm

SOLUTIONS

EXERCISE – I JEE MAIN

Sol.1 (a) $A + B \rightarrow C$

We have, first order in A and 0 order in B.

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^1[B]^0 = \frac{-d[A]}{dt} = -k[A]$$

For first order reaction, we know

$[A] = [A_0]\, e^{-kt}$

We have, at t = 1 hour

75% of A reacted

$$[A] = A_0 - 0.75A = \frac{1}{4}A_0$$

$$\frac{1}{4}[A_0] = [A_0]\, e^{-kt} \Rightarrow k = \ln 4$$

Now t = 2 hour,

$$\frac{[A]}{[A_0]} = e^{-2\times\ln 4} = \frac{1}{16}$$

$[A] = 6.25\,\%$ of A_0

$\therefore$ 6. 25% of A will be left unreacted

(b) Here, reaction is first order in both A and B

$$\therefore \text{Rate} = \frac{d[A]}{dt} = k[A]\,[B]$$

Since the initial concentration of A and B is the same and they have the same coefficient, their concentration will remain same of any time

$$\frac{-d[A]}{dt} = k[A]^2$$

$$\Rightarrow \int_{[A_0]}^{[A]} \frac{d[A]}{[A]^2} = \int_0^t -k\,dt$$

$$\Rightarrow -\frac{1}{[A]} + \frac{1}{[A_0]} = -k(t-0) = kt$$

At time t = 1 hour, $[A] = \dfrac{[A_0]}{4}$

$$\therefore -\frac{4}{[A_0]} + \frac{1}{[A_0]} = -k$$

$$\Rightarrow k = \frac{3}{[A_0]}$$

Now, at time t = 2 hours,

$$\frac{-1}{[A]} + \frac{1}{[A_0]} = -2.\frac{3}{[A_0]} = \frac{-6}{[A_0]}$$

$$\Rightarrow \frac{1}{[A]} = \frac{7}{[A_0]} \Rightarrow \frac{[A]}{[A_0]} = \frac{1}{7}$$

A left is $\dfrac{100}{7}$ % or $\boxed{14.3\,\%}$

(c) If the reaction is 0 order

$$\text{Rate} = \frac{d[A]}{dt} = k$$

$$\Rightarrow \int_{[A_0]}^{[A]} d[A] = \int_0^t k\,dt$$

$\Rightarrow\ [A] - [A_0] = -kt$

$\Rightarrow\ [A] = [A_0]\text{-}kt$

Now, at time t = 1 hour

$$[A] = \frac{[A_0]}{4}$$

$$\frac{[A_0]}{4} - [A_0] = -k$$

$$\Rightarrow k = \frac{3}{4}[A_0]$$

We see that, if t or [A] = 0

$$t = \frac{[A_0]}{k} = \frac{4}{3}\ \text{hours} < 2\ \text{hours}$$

The reactions will be finished before 2 hours and the 6 % of A will be left after 2 hours.

Sol.2 $CH_3-CH_2-\underset{(A)}{NO_2}+OH^- \rightarrow$

$CH_3–CH–NO_2 + H_2O$

Since this is a first order reaction

$[A] = [A_0]\, e^{-kt}$

Now, we have, at time t = $\dfrac{1}{2}$ minute,

$[A] = 0.99[A_0]$

($\because$1 % of nitroethane reacted)

$\therefore 0.99[A_0] = [A_0]\, e^{-k.\,1/2}$

$$\Rightarrow \frac{-k}{2} = \log_e(0.99)$$

$$\Rightarrow \frac{-k}{2} = 0.01\ \text{min.}$$

$\Rightarrow k = 0.02\ \text{min}^{-1}$

$\boxed{k = 2\times10^{-2}\ \text{min}^{-1}}$

Sol.3 Here, since the volume of liquid is negligible and as the liquid begins to form, pressure due to liquid will always be equal to

32. 5 mm Hg. Now, let initial pressure of P(g) be P_0 mm Hg, then according to stoichiometry

$$2P(g) \rightarrow 4Q(g) + R(g) + S(\ell)$$

at time

t = 0 min	P_0	0	0	0
t = 30 min	$P_0 - 2x$	4x	x	32. 5
$t = \infty$	0	$2P_0$	$\frac{P_0}{2}$	32. 5

Now, we are given, P_t = 317 mm Hg at t=30 min.

$\therefore P_0 - 2x + 4x + x + 32.5 = 317$

$\Rightarrow P_0 + 3x = 284.5$...(i)

at time, $t = \infty$ (very long time), P_t = 617 mm Hg

$\therefore 2P_0 + \frac{P_0}{2} + 32.5 = 617$

$\Rightarrow \frac{5P_0}{2} = 584.5$

$\Rightarrow P_0 = 233.8$ mm Hg

Putting this in (i), we get,

$3x = 284.5 - 233.8$

$\Rightarrow x = 16.9$

Now, since this is first order reaction, we have

$$k = \frac{2.303}{t} \log\frac{P_0}{P_p} = \frac{2.303}{30}\log\frac{233.8}{233.8(2\times16.9)}$$

$\Rightarrow k = 5.2 \times 10^{-3}\ \text{min}^{-1}$

Now, at t = 75 min, we have

$$k = \frac{2.303}{t}\log\frac{P_0}{P_p}$$

$\Rightarrow P_t = P_0 \times 10^{-kt/2.303}$

$= 233.8 \times 10^{\frac{-52\times10^{-3}\times75}{2.303}}$

P_t = 158. 22 m Hg

$\Rightarrow P_0 - 2x = 158.22$

$\Rightarrow x = \frac{233.8 - 158.22}{2} = 37.78$

Now, total pressure at t = 75 min

$P_t = P_0 + 3x + 32.5$

$= 233.8 + (3 \times 37.78) + 32.5$

$P_t = 379.55$ mm Hg

time fraction, $t_{7/8}$ is time at which $\frac{7}{8}$ th of reaction gets completed, ie. $P_\Delta = \frac{P_0}{8}$

Using rate law, $\frac{P_0}{8} = P_0 e^{-kt}$

$\Rightarrow t = \frac{2.303}{R}\log 8$

$\boxed{t = 399.96\ \text{min}}$.

Sol.4 We have, the reaction as,

$$B^{n+} \rightarrow B^{(n\text{-}2)t} + 4e$$

at time t=0 V_0 0

total time

t = 10 min $V_0 - x$ x

Now, for titration, we have

$B^{n+} + 2e \rightarrow B^{9n-2)+}$

From this, we see that for volume V_0 of B^{n+}, 2V volume of titrant is used.

at time t = 0, volume of titrant used = 25 mL

$\Rightarrow 2V_0 = 25$ mL

$\Rightarrow V_0 = 12.5$ mL

For titration of $B^{(n-1)+}$, we have

$B^{(n+4)t} + 5e \rightarrow B^{(n-1)e}$

i.e. for volume V of $B^{n+} + B^{(n+4))}$, 5V volume of titrant is used.

$\therefore$ at time t = 10 min,

Volume of titrant used = 32 mL

$\Rightarrow 2(V_0 - x) + 5x = 32$

$\Rightarrow 2V_0 + 3x = 32$

$\Rightarrow 3x = 32 - 25$

$\Rightarrow x = \frac{7}{3}$

Now, since this is a first order reaction, rate law is

$$k = \frac{2.303}{t}\log\frac{V_0}{V_{B^{n+}}} = \frac{2.303}{10}\log\frac{12.5}{12.5.x}$$

$$= 0.2303 \log\frac{12.5}{12.5.\frac{7}{3}}$$

$k = 0.0207\ \text{min}^{-1}$

Sol.5 We have initially, volume strength = 20

According to reaction

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

1 mole (34g) of H_2O_2 gives $\frac{1}{2}$ moles of O_2 i. e. 11. 21 at STP

Now, volume strength is the volume of O_2 given by unit volume of H_2O_2

Let normality of H_2O_2 = N

Then, $N = \dfrac{\text{weight}}{\text{Eq.weight}}$

$\Rightarrow$weight = 17 N (equivalent weight = 17)

Now, 34 g of H_2O_2 gives 11. 21 of O_2

$\therefore$17 N g of H_2O_2 gives $\dfrac{11.2 \times 17N}{34}$ of O_2

Volume strength = $\dfrac{11.2 \times 17N}{34}$ = 5. 6 N

Now, initially volume strength = 20

$\Rightarrow N_0 = \dfrac{20}{5.6} = 3.75$ N

At time, t = 6 hours, let normality be N.

Since, 10 mL of solution be diluted to 100 mL,

Now normality = $\dfrac{N.10}{100}$ = 0. 1 N

Now, since this is first order reaction, according to rate law, as N is proportional to number of moles of H_2O_2

$$k = \frac{2.303}{t}\log\frac{N_0}{N} = \frac{2.303}{6}\log\frac{3.57}{3.125}$$

$$\boxed{k = 0.022\ \text{hr}^{-1}}$$

Sol.6 We have for oxide film formation.

$$k = \frac{2.303}{6}\log\frac{\tau_{\max}}{\tau_{\max} - \tau}$$

where, $\tau_{\max}$ = maximum thickness of oxide film (at $t \to \infty$)

τ = thickness at time t

We are given

$\tau_{\max} = \dfrac{3.956}{1000}$ inch

$\tau = \dfrac{1.281}{1000}$ inch, at t = 6 weeks

$$k = \frac{2.303}{6}\log\frac{3.956}{3.956 - 1.281}$$

k = 0. 065

Now, when, $\tau = \dfrac{2.481}{1000}$ inch, we have

$$0.065 = \frac{2.303}{t}\log\frac{3.956}{3.956 - 2.481}$$

$$\Rightarrow t = \frac{2.303}{0.065} \times 0.49$$

t = 15. 13 weeks

t = 15. 13 weeks

longer = 9. 13 weeks

Sol.7 We have,

$$A \xrightarrow{H^+} B + C$$

Let initially x moles of A be present

$$A \xrightarrow{H^+} B + C$$

at t = 0 x 0 0

at t = ∞ 0 x x

We know optical rotation of B and C are 40° and –80° respectively at completion,

total optical rotation

$\Rightarrow$ 40x – 80x = -10

$\Rightarrow$ x = 0. 5

Now, optical rotation at t = 0

$\Rightarrow$ 60 × 0. 5

= 30°

Using first order rate law,

$$k = \frac{2.303}{t}\log\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$$

θ_0 = initial optical rotation

$$\text{or } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.303} + \frac{1}{\log\dfrac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}}$$

Putting values

$$t_{1/2} = \frac{0.693}{2.303} + \frac{20}{\log\dfrac{(30 - 1 - 20)}{(5 - 1 - 20)}}$$

since θ = 5°

at t = 20 min = $\dfrac{0.3 \times 20}{\log 2}$

$t_{1/2}$ = 20 min

Sol.8 Since, volume and temperature is constant, we take $P \propto n$

$$CH_3OCH_3(g) \to CH_4(g) + CO(g) + H_2(g)$$

at

t = 0 0. 4 0 0 0

t = 4.5hr. 0. 4–x x x x

We are given k = 4. 78 × 10^{-3}, since unit is min^{-1}. It is a first order reaction and

$P_A = P_0e^{-kt}$

= –4. 78 × 10^{-3} × 4. 5 × 60

$\Rightarrow P_A$ = 0. 7 e

0. 4 – x = 0. 11

$\Rightarrow$x = 0. 29

Now, at t = 4. 5hr, mean molecular mass, M_2

$$= \frac{(P_0 - x)M_{CH_3OCH_3} + x.M_{CH_4} + M_{CO} + x + M_0 + xM_{H_2}}{P - x + x + x + x}$$

$$= \frac{0.11 \times 46 \times 0.29 \times 16 + 0.29 \times 28 + 0.29 \times 2}{0.11 + 0.29 + 0.29 + 0.29}$$

$= 18.77$

at t = 0, molecular mass

$M_1 = M_{CH_3OCH_3} = 46$

$P_t = 0.4 - x + 3x = 0.4 \times 2x = 0.98$

According to Graham's law

Rate of diffusion $\propto \frac{P}{\sqrt{M}}$

$$\frac{D_0}{D_t} = \frac{P_0}{P_t}\sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{18.77}{46}} = \frac{0.4}{0.98}$$

$$\frac{D_0}{D_t} = 0.26$$

Sol.9 (a)According to Arrhenius equation, we have

$$\log\frac{k_2}{k_1} = \frac{E_A}{2.303}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Here, we have

$T_1 = (273 + 20)K = 293\ K$

$T_2 = (273 + 3)K = 276\ K$

$k_2 = \frac{k_1}{3}$

Putting values

$$\log\frac{1}{3} = \frac{E_A}{2.303 \times 8.314}\left(\frac{1}{293} - \frac{1}{276}\right)$$

$$\therefore E_A = \frac{+(\log 3 \times 2.303 \times 8.314 \times 293 \times 276)}{17}$$

$E_A = 43.46$ kJ/mol

(b)When $T_2 = (273 + 40)\ K = 313K$,

We have,

$$\log\frac{k_2}{k_1} = \frac{43.460}{303 \times 8.314}\left(\frac{1}{293} - \frac{1}{313}\right)$$

$\Rightarrow k_2 = 3312\ k_1$

Further, as $k \propto \frac{1}{t}$

$$\therefore \frac{t_2}{t_1} = \frac{k_1}{k_2} \Rightarrow t_2 = \frac{6.4}{3.12}$$

$\boxed{t_2 = 20.47 \text{ hours}}$

Sol.10 We have, according to Arrhenius equation

$$\log\frac{k_2}{k_1} = \frac{E_A}{2.303R}\left(\frac{1}{t_1} - \frac{1}{t_2}\right)$$

Here,

$E_A = 70\ \text{ks mol}^{-1}$

$t_1 = (273 + 25)\ K = 298\ K$

$t_2 = (273 + 40)\ K = 313\ K$

Putting values

$$\log\frac{k_2}{k_1} = \frac{70000}{2.303 \times 8.314}\left(\frac{1}{298} - \frac{1}{313}\right)$$

$\Rightarrow k_2 = 3.87\ k_1$

Now, equation

$A \to B$

According to rate law

$[A] = [A_0]\ e^{-kt}$

At T = 298 K, $k = k_1$, … t = 20 min,

$$[A] = \frac{3[A_0]}{4}$$

$$\therefore \frac{3}{4} = e^{-k_1.20}$$

$\Rightarrow k_1 = 0.014\ \text{min}^{-1}$

$\therefore k_2 = 3.87\ k_1 = 0.055\ \text{min}^{-1}$

Now, at T = 313 K, t = 20 min,

$k = 0.055\ \text{min}^{-}$

$[A] = [A_0]\ e^{-0.055 \times 20}$

$[A] = 0.3279\ [A_0]$

$\therefore$67.21 % of A got decomposed

Sol.11 We have, according to Arrhenius equation

$$\log\frac{k_2}{k_1} = \frac{E_A}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

For, $A \to$ products

if k at 310 K is taken to be k

Then, k at 300 K is $\frac{k}{2}$

Putting this in equation, we get

$$\log 2 = \frac{E_A}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$$

$$\Rightarrow E_A = \frac{\log 2 \times 2.303 \times 8.314 \times 310 \times 300}{10}$$

$E_A = 53.67$ kJ/mol

No we are also given at T = 310 K,

$t_{1/2} = 30$ min

$$\therefore k \text{ at } 310\ K = \frac{0.693}{t_{1/2}} = 0.0231\ \text{min}^{-1}$$

At 310 K, for (ii) $B \to$ products

k = 211 for (i)

= 0. 0462 min^{-1}

Further, for (ii)

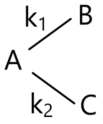
$$E_A = \frac{(E_A)}{2} = 26.\ 802 \text{ k J/mol}$$

Therefore, using Arrhenius equation, we get

$$\log \frac{k}{0.0769} = \frac{268.02}{2.303 \times 8.314}\left(\frac{1}{310} - \frac{1}{300}\right)$$

k = 0. 0327 min^{-1}

Sol.12 We are given,



here,

$$\frac{k_1}{k_2} = \frac{1}{9},\ k = 1.\ 3 \times 10^{-5}\ s^{-1}$$

Now, both are first order reactions

$$\therefore \frac{d[A]}{dt} = -(k_1 + k_2)[A]$$

$$\Rightarrow [A] = [A_0]\ e^{-(k_1+k_2)t}$$

Now, for A → C,

We have, $\frac{d[C]}{dt} = k_2[A]$

$$\Rightarrow \frac{d[C]}{dt} = k_2[A_0]\ e^{-(k_1+k_2)t}$$

$$\Rightarrow \int_0^{[C]} d[C] = k_2[A_0]\int_0^t e^{-(k_1+k_2)t}dt$$

$$[C] = \frac{k_2[A_0]}{k_1+k_2}(1 - e^{-(k_1+k_2)t})$$

$$\frac{[C]}{[A]} = \frac{k_2[A_0](1-e^{-(k_1+k_2)t})}{(k_1+k_2).[A_0]e^{-(k_1+k_2)t}}$$

$$= \frac{k_2}{k_1+k_2}(e^{(k_1+k_2)t} - 1)$$

Now, we have $k_1 = 1.\ 3 \times 10^{-5}\ s^{-1}$,

$k_2 = 9k_1 = 1.\ 17 \times 10^{-7}\ s^{-1}$

time, t = 1 hour = 36005

putting values,

$$\frac{[C]}{[A]} = \frac{9}{10}(e^{1.3\times10^{-4}\times3600} - 1)$$

$$\frac{[C]}{[A]} = 0.\ 537$$

Sol.13 As Cis-$(en)_2(OH)_2^+$ $\underset{k_b}{\overset{k_f}{\rightleftharpoons}}$ trans-$Cr(en)_2(OH)_2^+$

We have,

$$\text{eq. constant} = \frac{k_f}{k_b} = 0.\ 16$$

and $k_f = k_1 = 3.\ 3 \times 10^{-1}\ s^{-1}$

$$\Rightarrow k_b = \frac{k_t}{0.16}$$

$= 2.\ 0625 \times 10^{-4}\ s^{-1}$

Now using formula for eq. reactions.

$$\ln\left(\frac{x_{eq}}{x_{eq}.x}\right) = (k_f + k_b)\ t$$

We have to find t for which $x = \frac{x_{eq}}{q}$

$$\ln\left(\frac{x_{eq}}{x_{eq} - \frac{x_{eq}}{2}}\right) = (3.\ 3 \times 10^{-4} + 2.\ 0625 \times 10^{-3})t$$

$$\Rightarrow t = \frac{\ln 2}{2.3925 \times 10^{-5}}\ s$$

t = 289. 71 s

⇒t = 4. 83 min

Sol.14 We have, A $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ B

Also, we know, $k_{eq} = \frac{k_1}{k_2} = \frac{[B]_{eq}}{[A]_{eq}}$

$$\Rightarrow \frac{k_1}{k_2} = 4,\ k_1 = 10^{-2}\ s^{-1}$$

$$\Rightarrow k_2 = \frac{10^{-2}}{4} = 2.\ 5 \times 10^{-3}\ s^{-1}$$

Now at eq. , $[A] = [A_0] - x_{eq}$

$[B] = x_{eq}$

Then, $\frac{x_{eq}}{[A]e^{-x_{eq}}} = 4$

We are given $[A]_0 = 0.\ 01$ mole L^{-1}

$$\frac{x_{eq}}{0.01x_{eq}} = 1$$

$5x_{eq} = 0 + 60.\ 07$

$x_{eq} = 0.\ 008$ mole L^{-1}

Now, using equilibrium first order formula,

$$\ln\left(\frac{x_{eq}}{x_{eq} - x}\right) = (k_1 + k_2)t$$

At t = 30 s,

$$\text{In}\left(\frac{0.008}{0.008-x}\right) = (12.5\times10^{-3})\times 30 = -0.375$$

$\Rightarrow \quad x = 0.0025$ mole L^{-1}

Sol.15 We have,

$A(g) \rightleftharpoons B(g)$

For forward reaction, we have

$\Delta H = \Delta E = -33$ kJ/mol

We know,

$\text{In } k = \frac{-\Delta H^o}{RT}$ (since $\Delta S \approx 0$)

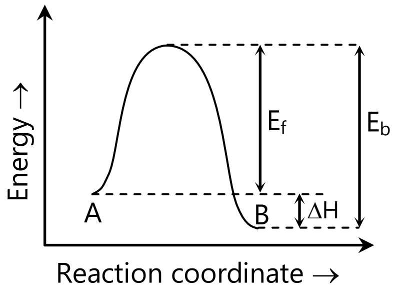
with T = 300 K, ΔH = 33 kJ/mol

we get, $k = \boxed{K = 5.57\times10^5}$

Now, we are given

$$\frac{E_f}{E_b} = \frac{20}{31}$$

Now, we have for this transformation



We see that

$E_b = E_f + |\Delta H|$

$\Rightarrow$ But $E_f = \frac{20E_b}{31}$

$\therefore E_b = \frac{20E_b}{31} + 33 \qquad \Rightarrow \frac{11E_b}{31} = 33$

$\Rightarrow E_b = 63$ kJ/mol

$E_f = E_b - 33$

$E_f = 30$ kJ/mol

Sol.16 We have

rate $k'[\text{complex}]^a$, $k' = k[H^+]^b$

Lets assume that this is Pseudo first order reaction, that is

a = 1

Then, we have, $t_{1/2} = \frac{0.693}{k'}$,

$t_{3/4} = \frac{1.386}{k'}$

We note that, here $t_{3/4} = 2.\,t_{1/2}$

which is true for given data also

Now, when, $[H^+] = 0.01$

$$t_{1/2} = 1 = \frac{0.693}{k'} = \frac{0.693}{k[H^+]^b}$$

$$\Rightarrow (0.01)^b = \frac{0.693}{k}$$

When $[H^+] = 0.02$

$$(0.02)^b = \frac{0.693}{k.t_{1/2}} = \frac{1.386}{k}$$

These both will be satisfied for b = 1.

$\therefore$ taking a = b = 1, all the given data can be verified and there are no contradictions

$\therefore$ a = b = 1

Sol.17 $A \xrightarrow{k_1} B$

$A \xrightarrow{k_2} C$

We have, k for disappearance of A,

$$\frac{-d[A]}{dt} = (l_1 + k_2)t$$

$\therefore k = k_1 + k_2$

Using Arrhenius equation,

$$Ae^{\frac{-E}{RT}} = A_1e^{\frac{-E_1}{RT}} + A_2e^{\frac{-E_2}{RT}}$$

A = pre exponential constant

Differentiating with respect to $\frac{1}{T}$, we get

$$\frac{-AE}{R}e^{\frac{-E}{RT}} = \frac{-A_1E_1}{R}e^{\frac{-E_1}{RT}} - \frac{-A_2E_2}{R}e^{\frac{-E_2}{RT}}$$

$\Rightarrow Ek = E_1k_1 + E_2k_2$

$$\Rightarrow E = \frac{E_1k_1 + E_2k_2}{k}$$

$$\Rightarrow \boxed{E = \frac{E_1k_1 + E_2k_2}{k_1 + k_2}}$$

Sol.18 (a)We have,

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$$

$C \xrightarrow{k_1} D$

since second step is RDS,

Rate = $k_3[C]$

Also, $\frac{d[C]}{dt} = -k_3[C] + k_2[A][B] - k_2[C]$

Now, at steady state, $\frac{d[C]}{dt} = 0$

$$\Rightarrow [C] = \frac{k_1[A][B]}{k_3 + k_2}$$

$$\therefore \text{Rate} = \frac{k_1k_3[A][B]}{k_3 + k_2}$$

(b)If $k_2 >> k_3$, then $k_2 + k_3 \simeq k_2$

then, Rate = $\frac{k_1k_3}{k_2}$[A] [B]

Using Arrhenius equation,

$$k = A\ e^{\frac{-E_A}{RT}}$$

$$k = \frac{A_1 e^{\frac{E_{a_1}}{RT}} A_3 e^{\frac{E_{a_3}}{RT}}}{A_2 e^{\frac{E_{a_2}}{RT}}} = \frac{A_1A_3}{A_2} e^{\frac{-(E_{a_1}+E_{a_3}-E_{a_2})}{RT}}$$

Comparing with $k = Ae^{\frac{-E_a}{RT}}$

$$\boxed{A = \frac{A_1A_3}{A_2}}$$

$$\boxed{E_a = E_{a_1} + E_{a_3} - E_{a_2}}$$

Sol.19 We have,

Rate,R = k_3[COCl] [Cl_2]

(∵ (iii) is slowest step (RDS))

Also, from equilibrium of (ii),

$$\frac{k_2}{k_{-2}} = \frac{[COCl]}{[CO][Cl]}$$

and from equilibrium of (i),

$$\frac{k_1}{k_{-1}} = \frac{[Cl]^2}{[Cl_2]}$$

$$[Cl] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} ([Cl_2])^{1/2}$$

Putting these values back in rate formula, we get

Rate

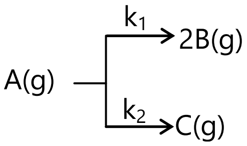
$$= k_3 \frac{k_2}{k_{-2}} [CO] \left(\frac{k_1}{k_{-1}}\right)^{+\frac{1}{2}} ([Cl_2])^{1/2} [Cl]$$

$$\frac{d[COCl_2]}{dt} = k_3 \frac{k_2}{k_{-2}} \frac{k_1}{k_{-1}} [CO][Cl_2]^{3/2}$$

$$= k[CO]\ [Cl_2]^{3/2}$$

$$k = k_3 \cdot \frac{k_2}{k_{-2}} \left(\frac{k_1}{k_2}\right)^{1/2}$$

Sol.20



We have,

$$\text{Rate} = \frac{-d[A]}{dt} = -(k_1 + k_2)[A]$$

$[A] = [A]_0\ e^{-kt}$, ;$k = k_1 + k_2$

Further, Rate = $\frac{1}{2}\frac{d[B]}{dt} = k_1[A]$

Putting value of [A] and integrating

$$[B] = \frac{2k_1[A_1]}{k_1 + k_2}(1 - e^{-kt})$$

Similarly, $[C] = \frac{k_2[A]_0}{k_1 + k_2}(1 - e^{-kt})$

Now, we are given $[A]_0$ = 1 atm

At t → ∞, P_t = 1. 5 atm

Putting values and taking t = ∞, we get

$$\frac{2k_1}{k_1 + k_2} + \frac{k_2}{k_1 + k_2} = 1.5$$

$\Rightarrow 2k_1 + k_2 = 1.5\ k_1 + 1.5k_2$

$\Rightarrow k_1 = k_2 = \frac{k}{2}$

Now, taken at t = 10s, P_t = 1. 4 atm

$$\therefore [A]_0 e^{-k.10} + \frac{k[A]_0}{k}(1 - e^{-k.10})$$

$$+ \frac{k[A]_0}{2k}(1 - e^{-k.10}) = 1.7$$

$[A]_0$ = 1,

$$\therefore e^{-10R} + 1 - e^{-10R} + \frac{1}{2} - \frac{e^{-10k}}{2} = 1.4$$

$\Rightarrow e^{-10}R = 0.2$

$\Rightarrow k = 0.16$

$\Rightarrow k_1 = k_2 = \frac{k}{2} = 0.08$

Sol.21 For 50% completion, time taken

$$t_{1/2} = \frac{0.693}{k}$$

$$\Rightarrow k = \frac{0.693}{69.3} = 0.01\ \text{min}^{-1}$$

Now, for 80%, [A] = 0. 2[A_0]

Using $[A] = [A]_0 e^{-RT}$

$\Rightarrow 0.2 = e^{-RT}$

$$\Rightarrow t = \frac{\ln 5}{0.01}$$

t = 161 min

Sol.22 We have, from Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Now, $\frac{k_2}{k_1} = 4$, $T_1 = 27°C = 300$ K

$T_2 = 47°C = 320$ K

Putting values, we find

$$\log 4 = \frac{E_A}{2.303\times 8.314}\left[\frac{1}{300}-\frac{1}{320}\right]$$

$$\Rightarrow E_A = \frac{2\log 2\times 320\times 300\times 2.303\times 8.314}{20}$$

$E_A = 55.33$ kJ mol^{-1}

Sol.23 $2A + B + C \rightarrow D + 2E$

(i) Since, this is first order w. r. t. A, second order w. r. t. B, and 0 order w. r. t. C.

Rate law = $k[A]\,[B]^2[C]^2$

Rate, $R = k[A]\,[B]^2$

(ii) Now rate, $R' = k[2A]\,[2B]^2$

$= 8k[A]\,[B]^2 = 8k$

$\therefore$ Rate becomes 8 times

Sol.24 We know, for first order reaction

$$k = \frac{2.303}{30}\log\frac{[A]_0}{[A]_t}$$

At T = 27°C = 300 K, at t = 30 min, 50% of reaction gets completed, i. e. $[A]_t = 0.5[A]_0$

$$k = \frac{2.303}{30}\log 2$$

$k = 0.0231$ min^{-1}

$= 3.85 \times 10^{-4}$ s^{-1}

At T = 47°C = 320 K, time taken for 50% completion is 10 min.

$$\therefore k = \frac{2.303}{10}\log 2$$

$k = 0.0693$ min^{-1}

$= 11.55 \times 10^{-4}$ s^{-1}

Now, by Arrhenius equation

$$\ln\frac{k_2}{k_1} = \frac{E_A}{2.303}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

At T = 300 K, k = 0.0231 min^{-1}

T = 320 K, k = 0.0693 min^{-1}

Putting values

$$\log\frac{0.0693}{0.0231} = \frac{E_A}{2.303\times 8.314}\left(\frac{1}{300}-\frac{1}{320}\right)$$

$E_A = 43.78$ kJ/mol

Sol.25 Firstly, we assume that reaction is first order and see if the data is consistent.

For first order reaction, we have

$$k = \frac{2.303}{t}\log\frac{\theta_0-\theta_\infty}{\theta_t-\theta_\infty}$$

At time, t = 10 min,

$$k = \frac{2.303}{t}\log\frac{32.4-(-11.1)}{28.8-(-11.1)}$$

$k = 8.14 \times 10^{-3}$ min^{-1}

At time, t = 20 min

$$k = \frac{2.303}{t}\log\frac{(32.4+11.1)}{25.5-(-11)}$$

$k = 8.64 \times 10^{-3}$ min^{-1}

At time, t = 30 min

$$k = \frac{2.303}{t}\log\frac{32.4-(11.1)}{22.4-(-11)} = 8.70 \times 10^{-3}\ \text{min}^{-1}$$

At t = 40 min,

$$k = \frac{2.303}{40}\log\frac{32.4-(11.1)}{19.6-(-11.1)} = 8.71 \times 10^{-3}\ \text{min}^{-1}$$

We see that all values of k are pretty close to each other,

$\therefore$ the reaction is first order.

Sol.26 We know, for nth order reaction

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

Here as $[A]_0$ is doubled, $t_{1/2}$ gets halved,

$$\therefore t_{1/2} \propto \frac{1}{[A]_0}$$

or $n - 1 = 1$

$\Rightarrow n = 2$

Hence, second order reaction.

Sol.27 We have, by Arrhenius equation

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303k}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Now, given data,

at t = 50°C = 323 K,

$k = 1.5 \times 10^{+7}$ sec^{-1}.

at T = 100°C = 373 K,

$k = 4.5 \times {}^{+7}$ sec^{-1}

Filling the data,

$$\log 3 = \frac{E_a}{2.303\times 8.314}\left(\frac{1}{323}-\frac{1}{373}\right)$$

$$E_a = A\,e^{\frac{-E_a}{RT}}$$

$E_a = 2.2 \times 10^7$ J mol^{-1}

$$\text{Now, } k = A\,e^{\frac{-E_a}{RT}}$$

$\Rightarrow A = k\, e^{\frac{+E_a}{RT}}$

$= 1.5 \times 10^{+7}\ e^{\frac{+2.2\times10^{7}}{8.214\times323}}$

$A = 5.42 \times 10^{10}\ s^{-1}$

Sol.28 Rate = k[A]

(i)Initial rate = $k[A]_0$

$= 1.8 \times 10^{-2} \times 0.1$

$= 1 \times 10^{-3}$ mol sec^{-1} L^{-1}

(ii)After 60 sec (1 min),

Rate = $k[A]_1$

$= k[A]_0\, e^{-k\times60}$

$= 5.495 \times 10^{-3}$ mol sec^{-1} L^{-1}

Sol.29 Since, unit of rate constant is min^{-1}, it is first order reaction

Initial rate = $k\,[A]_0$

$= 10^{-3} \times 0.2$

$= 2\times10^{-4}$ mol min^{-1} dm^{-3}

After 200 minutes,

$[A] = [A]_0\ e^{-10^{-3}\times200}$

$= 0.8187[A]_0$

$\therefore$ 18.12 % of reactant converted into product.

Sol.30 (i)At time, t = 10 min, $[A] = 0.8\,[A]_0$

$\therefore\ 0.8[A]_0 = [A]_0\, e^{-10k}$

$\Rightarrow k = 0.022$ min^{-1}

(ii)When 75% reaction is completed,

$[A] = \frac{1}{4}[A]_0,$

$\therefore \frac{1}{4}[A]_0 = [A]_0\, e^{-0.022t}$

$\Rightarrow t = 63.01$ min.

EXERCISE – II JEE MAIN

Sol.1 [B] From the table, we see that when [A] is doubled, rate get becomes 4 times, keeping [B] constant

$\therefore$rate $\propto [A]^2$

Also, when [B] is doubled, keeping [A] doubled. Rate becomes 2 times

$\therefore$rate $\propto [B]$

$\therefore$rate $= k[A]^2[B]$

Sol.2 [A] Rate, $r_i = k[A]^n[B]^m$

$r_f = k[2A]^n[B/2]^m = \frac{k\,2^n}{2^m}[A]^n[B]^m$

$\frac{r_f}{r_i} = 2^{(n-m)}$

Sol.3 [A] We have $t_{1/2}$ = 15 min (0. 8 M→0. 4M)

Now, for 0. 1 M to 0. 025 M,

$t = 2 \times t_{1/2}$

= 30 min

$(0.\ 1 \xrightarrow{t_{1/2}} 0.\ 5 \xrightarrow{t_{1/2}} 0.\ 025)$

Sol.4 [D] Only statement (D) is correct as k is constant at a given temperature.

(A) and (B) are correct for first order reaction. (C) is wrong as

$\frac{d[C]}{dt} = -\frac{1}{2}\frac{d[A]}{dt}$ (not $2\frac{d[A]}{dt}$]

Sol.5 [D] For a first order reaction,

$[A] = [A]_0e^{-kt}$

When, $[A] = \frac{3}{4}[A]_0$, $t = t_{3/4}$

$\Rightarrow \frac{3}{4} = e^{-k.t_{3/4}}$

$\Rightarrow t_{3/4} = \frac{0.29}{k}$

Sol.6 [D] rate $\propto [O]^2$

$\therefore$ when [(O)] is doubled, rate becomes 4 times.

Sol.7 [C] $A + 3B \rightarrow P$

$\Delta H = 2x$ kJ/mole of A . . (i)

$M \rightarrow 2Q + R$

ΔH = tx k J/mole of M...(ii)

We see that, if these reactions are carried simultaneously energy released from (i) and energy absorbed is (ii) counter each other further, ΔH = 2OH, rate of second reaction will be double of that of (i)

Now, rate of (ii), (i) $= \frac{-1}{3}\frac{d[B]}{dt} = \frac{y}{3}$

rate of second $= \frac{2y}{3} = \frac{1}{2}\frac{d[Q]}{dt}$

$\Rightarrow \frac{d[Q]}{dt} = \frac{4}{3}y$

Sol.8 [B] We have t = 138. 6 min for

1M → 0. 25 M

i.e., $2t_{1/2} = 138.\ 6 = \frac{2 \times 0.693}{k}$

$(\because 1 \xrightarrow{t_{1/2}} 0.\ 5 \xrightarrow{t_{1/2}} 0.\ 25)$

$\Rightarrow k = 0.\ 01$

When [A] = 0. 1,

rate = k[A]

$= 0.\ 01 \times 0.\ 1$ M min^{-1}

$= 10^{-3}$ M min^{-1}

Sol.9 [B] For zero order reaction, rate is always constant.

i. e. rate = 10^{-2} M min^{-1}

	$A(g) \rightarrow$	$2B(g)$
t=0	0. 1	
t= 1	0. 1–x	2x

$\frac{1}{2}\frac{d[B]}{dt} = 10^{-2}$

[B] = 0. 02 t

At t = 60 sec = 1 minute

[B] = 0.02 M

Sol.10 [D] Let time be t

then, for $X \xrightarrow{k_1} A + B$

50% reaction gets completed at time t

$\Rightarrow \frac{1}{2}[X]_0 = [X]_0\ e^{-k_1t}$

$k_1 = \frac{\ln 2}{t}$

For $Y \xrightarrow{k_2} C + D$

96 % of reaction gets completed at time t.

$\therefore 0.04[Y]_0 = [Y]_0\ e^{-k_2 t}$

$k_2 = \dfrac{\ln 25}{t}$

$\dfrac{k_2}{k_1} = \dfrac{\ln 25}{\ln 2} = 4.65$

Sol.11 [D] We know, for nth order reaction

$t_{1/2} \propto \dfrac{1}{P_0^{n-1}}$

$\Rightarrow \dfrac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\dfrac{P_{O_1}}{P_{O_2}}\right)^{n-1}$

Putting values,

$\dfrac{950}{235} = \left(\dfrac{500}{250}\right)^{n-1}$

$\Rightarrow n - 1 = \dfrac{\log 4.04}{\log 2} = 2$

$\Rightarrow n = 3$

Sol.12 [C] We have first order reaction

$k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$

at $t = 20$ min, $[A]_t = 0.8\,[A]_0$

(since 20% reaction completed)

$\Rightarrow k = \dfrac{2.303}{20}\log\dfrac{5}{4}$

$k = 1.11 \times 10^{-2}\ \text{min}^{-1}$

$t_{1/2} = \dfrac{0.693}{k} = 62.13$ minutes

Sol.13 [C] Rate = k[A]

$= k[A]_0 e^{-kt}$

It follows an exponential decay

Sol.14 [D] $A(g) \rightarrow 2B(g)$

We have, $k_{eq} = \dfrac{[B]^2}{[A]} = \dfrac{[100/V]^2}{[10^{-5}/V]}$

$= \dfrac{10^4}{10^{-5}} \cdot \dfrac{1}{10} = 10^8$

$10^8 = \dfrac{k_f}{k_b} = \dfrac{1.5\times10^{-3}}{k_b}$

$\Rightarrow \boxed{k_b = 1.5 \times 10^{-11}\ \text{L mol}^{-1}\ \text{s}^{-1}}$

Sol.15 [B] $A + B \rightarrow C + D$

t = 0 1 1 0 0

t = 1 1-x 1–x x x

We have,

$\text{Rate} = \dfrac{-d[A]}{dt} = k[A]^{1/2}[B]^{1/2}$

$\Rightarrow \dfrac{-d[A]}{dt} = k(1-x)^{1/2}\,(1-x)^{1/2}$

$\Rightarrow \dfrac{-d[A]}{dt} = k(1-x)$

This can be written as,

$\dfrac{-d[A]}{dt} = k[A]$

$\Rightarrow [A] = [A]_0 e^{-kt}$

when $[A] = 0.25[A]_0$

$t = \dfrac{2\ell n2}{k} = \dfrac{2\times2.303\log 2}{2.303\times10^{-3}}$

$\boxed{t = 600\ \text{s}}$

Sol.16 [A] We have for first order,

$[A] = [A]_0 e^{-kt}$

$[A]_0 = \dfrac{0.1}{2}\ \text{mol L}^{-1} = 0.05\ \text{mol L}^{-1}$

$k = 3.465 \times 10^{-6}\ \text{s}^{-1}$, $t = 200$ s

$[A] = 0.05\ e^{-3.465\times10^{-6}\times200}$

≈ 0.05 M

Sol.17 [D] R is universal gas constant

k is rate constant

A is pre exponential factor

E_a is activation energy

Sol.18 [C] This is the correct definition.

Sol.19 [B] $k = A\,e^{-E_0/RT}$;As $T \rightarrow \infty$,

$k = A = 6 \times 10^{14}\ \text{s}^{-1}(\because\ e^{-E_0/RT} \rightarrow 1)$

Sol.20 [B] We have, from Arrhenius equation

$\log\dfrac{k_2}{k_1} = \dfrac{E_A}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

Here, at $T_1 = 27°C = 300$ K

$k_1 = \dfrac{0.693}{20}\ \text{min}^{-1}$

at$T_2 = 47°C = 320$ K

$k_2 = \dfrac{0.693}{5}\ \text{min}^{-1}$

Putting these values,

$$\log 4 = \frac{E_A}{2.303\times8.314}\left(\frac{1}{300}-\frac{1}{320}\right)$$

$\Rightarrow \boxed{E_A = 55.14\ \text{kJ/mol}}$

Sol.21 [C]

We have, 27°C = 300 K, 3. 8 × 10^{-16} of reactant molecules exist in the activated region.

i. e, $N = 3.8 \times 10^{-18} N_0$

Now, $N = N_0 e^{-E_a/RT}$

$$E_a = RT\log_e\frac{N_0}{N} = 8.314 \times 300 \log_e\frac{N_0}{3.8\times10^{-18}N_0}$$

E_a = 100 kJ/mol

Sol.22 [D] Since, at 400 K, 0. 0001% (10^{-4}%) of collisions are effective only 10^{-4}% of molecules have their energy above activation energy.

$$E_a = 2.303\,RT\log\frac{N_0}{N}$$

$$= 2.303 \times 8.314 \times 400 \log\frac{N_0}{10^{-6}N_0}$$

= 45. 944 k J/mol = 11. 05 k cal/mol

Sol.23 [A, C, D]

(A)Unit of A = Unit of k ≠ mol $L^{-1}s^{-1}$

(B)Order of an elementary must atleast be 1 (atleast 1 molecule should be present)

(C) Molecularity can be defined for any elementary reaction

(D) Decay constant (λ) of radioactive substance is independent of temperature

Sol.24 [A, C] With increase in $[A]_0$, rate will increase, leading to increase in yield of B. A → B has higher E_a, which means it has lower k and thus with increase in temperature k_1 will increase more than k_2, resulting in increase in yield of B.

Sol.25 [A, B, C]

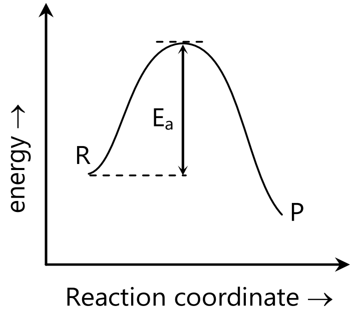
(D) A zero order reaction is always complex, rest all are correct.

Sol.26 [C] For reactions with order ≤ 1, time of completion can be determined as those reactions gets fully completed in specific amount of time.

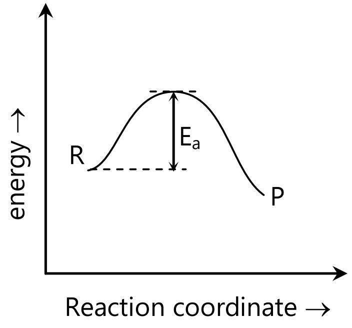
For reactions with order > 1, reaction never goes to 100 % completion and hence time of completion cannot be determined.

Sol.27 [A]

Without catalyst



With catalyst



Paragraph-1

We have

$$\frac{df}{dt} = l(1-f)$$

$$\int_0^f\frac{df}{1-f} = \int_0^f k\,dt$$

$$-\ln(1-f)_0^f = kf\big|_0^f$$

$-\ln(1-f) = kt$

$f = 1 - e^{-kt}$

Sol.28 [B] Slope of ln(1 – f) vs f graph

$$= -k = \frac{-3}{200}\ \text{hr}^{-1}$$

$$\Rightarrow k = \frac{3}{200}\ \text{hr}^{-1}$$

When $f = \frac{1}{2}$

$$\frac{1}{2} = 1 - e^{-kt}$$

$$t = \frac{\ell n2}{k} = \frac{0.693\times200}{3} = 46.2\ \text{hrs.}$$

Sol.29 [A] $f = 1 - e^{-kt}$

$f = [1 - e^{-3t/200}]$

Paragraph-2

Sol.30 [C] For $t = 100$ min, $x = \frac{3}{4}a$

$$\therefore k = \frac{1}{100}\ln\frac{a}{a-\frac{3}{4}a} = \frac{\ell n2}{50}\,\text{min}^{-1}$$

When $x = 0.9\,a$,

$$k = \frac{1}{t}\ln\frac{a}{a-0.9a}$$

$$t = \frac{1}{k}\ln 10 = \frac{50\ln 10}{\ln 2} = \frac{50}{\ln 2} = \frac{50}{0.3}$$

$= 166.66$ min

Sol.31 [B] $[A]_0 = \frac{2}{12.5} = 0.16$

We have,

$$\frac{1}{3}\frac{d[B]}{dt} = k[A]$$

	$A(g) \rightarrow$	$3B(g)$ +	$2C(g)$
at time 0	0.16		
at time t	0.16–x	3x	2x

Also, $\frac{d[A]}{dt} = -k[A]$

$[A] = [A]_0\, e^{-kt}$

$= 0.16\; e^{1.386\times10^{-2}\times100}$

$= 0.04$

i. e. , $0.16 - x = 0.04$

$x = 0.12$

$[B] = 3x = 0.36.$

PREV YEARS' QUESTIONS JEE MAIN

Sol.1 (a) $\frac{1}{2}A \rightarrow 2B\,;\; -2\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$;

$-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$

Sol.2 (c) $\frac{\text{Rate at }50°C}{\text{Rate at}T_1°C} = (2)^{\frac{\Delta T}{T_1}} = (2)^{\frac{50}{10}}$

$= 2^5$ = 32 times

Sol.3 (c) $k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$;

$t = 2 \times 10^2$, a = 800, a – x = 50

$k = \frac{2.303}{2\times10^2}\log_{10}\frac{800}{50} = \frac{2.303}{2\times10^2}\log_{10}16$

$= \frac{2.303}{2\times10^2}\log_{10}2^4 = \frac{2.303}{2\times10^4} \times 4 \times 0.301$

$= 1.38 \times 10^{-2}\ s^{-1}$

Sol.4 (a) 2A + B → Product

When conc. of B is doubled, the half life did not change, hence reaction is of first order w.r.t. B. When concentration of A is doubled, reaction rate is doubled, hence reaction is of first order w.r.t. A,

Hence, over all order of reaction is 1 +1 = 2

So, unit of rate constant mol^{-1} lit s^{-1}.

Sol.5 (d) Rate= $k(N_2O_5)$ hence 2.4×10^{-5}

$= 3.0 \times 10^{-5}(N_2O_5)$ or (N_2O_5)

$= 0.8$ mol l^{-1}

Sol.6 (c)In first order reaction for x% completion

$k = \frac{2.303}{t}\log\left(\frac{100}{100-x\%}\right)$

$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\left(\frac{100}{100-99}\right)$

$= \frac{0.693}{6.93} = \frac{2.303\times2}{t}$

So, t = 46.06 min.

Sol.7 (b) Because two molecules are taking part in elementary

Sol.8 (c) Since $-\frac{dx}{dt} \propto [CO]^2$ so on doubling the concentration of CO, the rate of reaction will increase by 4 times.

Sol.9 (a) $R = k[A][B]^2$ order of reaction =2+1= 3

Sol.10 (d) The differential rate law for, $NO + Br_2 \longrightarrow NOBr_2$ would be

$-\frac{dc}{dt} = k[NOBr_2][NO]$

We have, $K_c = \frac{[NOBr_2]}{[NO][Br_2]}$

Provided the first reaction attains equilibrium rapidly.

$\therefore -\frac{dc}{dt} = k \times k_c \times [NO]^2[Br_2]$

$= k[NO]^2[Br_2]$

∴The order of the reaction with respect to NO(g) is 2.

Sol.11 (a) For A

Rate = $k(Cl_2)(H_2S)$ (By slow step)

For B

Rate = $k[Cl_2][HS^-]$

$k_{eq} = \frac{[H^+][HS^-]}{[H_2S]}$

(according to equilibrium)

Rate = $k[Cl_2]\,\frac{k_{eq}[H_2S]}{[H^+]}$

Rate = $kk_{eq}[Cl_2]\,\frac{[H_2S]}{[H^+]}$.

Sol.12 (d) $t_{1/2} = \frac{a}{2k_0}$ (for zero order reaction)

$k_0 = \frac{a}{2\times t_{1/2}} = \frac{2}{2\times1} = 1$

$k_0 = \frac{A_0 - [A]_t}{t} \Rightarrow k_0 = \frac{0.50 - 0.25}{t} = 1$

$\boxed{t = 0.25\text{ hr}}$.

Sol.13 (d) So,

$\Delta H_{\text{Reaction}} = E_f - E_b = 80 - 100 = -20$.

Sol.14 (a) For endothermic reaction $\Delta H = +ve$

Then from equation

$\Delta H = E_{aF.R} - E_{aB.R}$; $E_{B.R} < E_{F.R}$.

Sol.15 (b) In photochemical reaction, the rate of formation of product is directly proportional to the intensity of absorbed light.

EXERCISE – I JEE ADVANCED

Sol.1 $4NH_3(g) + 5O_2(g)$

$\rightarrow 4NO(g) + 6H_2O(g)$

Rate of reaction

$$= \frac{-1}{4}\frac{d[NH_3]}{dt} = \frac{-1}{5}\frac{d[O_2]}{dt}$$

$$= \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$$

(i)Rate of reaction = $\frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{4}\frac{1.08\times10^{-2}}{3}$

$= 9 \times 10^{-4}$ mol L^{-1}

(ii) $\frac{-d[NH_3]}{dt} = \left|\frac{+4}{4}\frac{d[NO]}{dt}\right|$

$= \frac{+1.08}{3}\times10^{-2} = 3.6 \times 10^{-3}$ mol L^{-1}

(iii) $\frac{d[H_2O]}{dt} = \frac{6}{4}\frac{d[NO]}{dt}$

$= \frac{3}{2}\times\frac{1.08\times10^{-2}}{3} = 5.4 \times 10^{-3}$ mol L^{-1}

Sol.2 (a)$2H_2O_2 \rightarrow 2H_2O + O_2$

We know,

$$\frac{-1}{2}\frac{d[H_2O_2]}{dt} = \frac{-1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{d[H_2O]}{dt} = 2\frac{d[O_2]}{dt}$$

$= 2 \times 3.6$ M min^{-1}

$\frac{d[H_2O]}{dt} = 7.2$ M min^{-1}

(b) $\frac{-d[H_2O_2]}{dt} = \frac{2}{2}\frac{d[H_2O]}{dt}$

$= \frac{-d[H_2O_2]}{dt} = 7.2$ M min^{-1}

Sol.3 $N_2 + 3H_2 \rightarrow 2NH_3$

(a) $\frac{d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

$\frac{-d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

$= \frac{1}{2} \times 2 \times 10^{-4}$ mol $L^{-1}s^{-1} = 10^{-4}$ mol L^{-1} s^{-1}

(b) $\frac{-d[H_2]}{dt} = \frac{3}{2}\times\frac{d[NH_3]}{dt}$

$= \frac{3}{2}\times 2 \times 10^{-4}$ mol L^{-1} $s^{-1} = 3 \times 10^{-4}$ mol L^{-1} s^{-1}

Sol.4 (i) Reaction of first order in A, second order in B and 0 order w. r. t. C.

$\frac{dx}{dt} = k[A]^1[B]^2[C]^0$, $k = [D]_t$

$\Rightarrow \frac{dx}{dt} = k[A][B]^2$

(ii)If [A] , [B] , [C] are all doubled.

$r_f = k[2A][2B]^2 = 8k[A][B]^2 = 8r$

Rate becomes 8 times

Sol.5 We have, by ideal gas equation

PV = nRT

$\Rightarrow P = \frac{n}{V}RT$

P = CRT

$C = \frac{P}{RT}$

Rate of reaction = $\frac{\Delta C}{\Delta t} = \frac{1}{RT}\frac{\Delta P}{\Delta T}$

We have, R = 0. 0921 L atm/mol. k

T = 27°C = 300 K

$\Delta P = (2 - 1.1)$ atm $= 0.9$ atm

$\Delta T = 75 \times 605 = 45005$

Rate of reaction

$= \frac{1}{0.0921\times300}\times\frac{0.9}{75\times60}$ Ms^{-1}

$= 8.12 \times 10^{-6}$ Ms^{-1}

Rate of reaction in terms of pressure

$= \frac{\Delta P}{\Delta t} = \frac{0.9}{75}$ atm $min^{-1} = 0.012$ atm min^{-1}

Sol.6 $2A + B_2 \rightarrow 2AB$

Since, this is an elementary reaction,

rate, $r_i = k[A]^2[B_2]$

If volume of vessel reduced to one-third, [A] and $[B_2]$ becomes 3 times each.

$\therefore r_f = k[3A]^2[3B_2] = 27k[A]^2[B_2] = 27r_i$

Hence, rate becomes 27 times.

Sol.7 $3BrO^- \rightarrow BrO_3 + 2Br^-$

We have,

Rate $= \frac{-1}{3}\frac{\Delta[BrO]}{\Delta t} = \frac{\Delta[BrO_3^-]}{\Delta t}$

$= \frac{1}{2}\frac{\Delta[Br]}{\Delta t} = k[BrO^-]^{+2} = \frac{-\Delta[BrO^-]}{\Delta t} = 3k[BrO^-]^2$

We have, 3k = 0.056

$k = 0.0186\ mol^{-1}\ s^{-1}$

(a) $\frac{\Delta[BrO_3^-]}{\Delta t} = k[BrO^-]^2 = 0.0186[BrO^-]^2$

hence rate constant $= 0.0186\ L\ mol^{-1}s^{-1}$

(b) $\frac{\Delta[Br^-]}{\Delta t} = 2k[BrO^-]^2 = 0.037[BrO^-]^2$

rate constant $= 0.037\ Lmol^{-1}s^{-1}$

Sol.8 We have,

$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

$\Rightarrow \frac{-d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$

$= \frac{1}{1/2}\frac{d[O_2]}{dt} = +k[N_2O_5]$

Hence, $k_1 = k$, $k_2 = 2k$, $k_3 = \frac{k}{2}$

$\Rightarrow k_1 = \frac{k_2}{2} = 2k_3 \Rightarrow 2k_1 = k_2 = 4k_3$

Sol.9 $4\ {}_1^1H \rightarrow {}_2^4He\ \Delta H = 2.6$ MeV

It means 4 atoms of H, eject 26 MeV energy.

Energy released by 1 mole of

$H = \frac{N_A}{4} = 26 \times 10^6 \times 1.6 \times 10^{-14}$ J

$= 6.26 \times 10^{11}$ J

Power output of sun $= 3.9 \times 10^{26}$ W

$= 3.9 \times 10^{26}$ J/s

i. e. it radiates 3.9×10^{26} J in one second.

Number of moles of H required per second

$= \frac{3.9 \times 10^{26}}{6.26 \times 10^{11}} = 6.23 \times 10^{14}$

Total moles of H on sun

$= \frac{1.7 \times 10^{30}}{10^{-3}} = 1.7 \times 10^{33}$

Time taken $= \frac{1.7 \times 10^{33}}{6.23 \times 10^{14}} = 2.72 \times 10^{18}$ s

Sol.10 $A(g) + 2B(g) \rightarrow C(g) + D(g)$

t = 0 0. 6 0. 8 0 0

t 0. 6–x 0. 8–2x x x

Since this is elementary reaction

Rate, $r = k[B]^2[A]$

Now, $r_i = k(0.6)(0.8)^2 = 0.381\ k$

When $P_i = x - 0.2$ atm

$P_A = 0.6 - x = 0.4$ atm

$P_B = 0.8 - 2x = 0.8 - 0.4 = 0.4$ atm

$r_f = k(0.4)(0.4)^2 = 0.064\ k$

$\frac{r_f}{r_i} = \frac{0.064}{0.384} = \frac{1}{6}$

Sol.11 A → B

$k = 1.2 \times 10^{-2}\ Ms^{-1}$

Since unit of rate constant is Ms^{-1}, it is zero order reaction

Rate law [B] = kt

At t = 10 min

$[B] = 1.2 \times 10^{-2} \times 10 \times 60$ M

[B] = 7. 2 M

At t = 20 min

$[B] = 1.2 \times 10^{-2} \times 20 \times 60$ M

= 14. 4 M

But, $[A]_0 = 10$ M and [B] cannot be greater than $[A_0]$ $[A]_0$.

∴ [B] = 14.4 M implies that reaction has reached completion, i. e.

$[B]_{max} = 10$ M

[B] = 10 M

Sol.12 For zero order reaction,

$[A] = [A]_0 - kt$

At t = 0, $[A] = [A]_0 = 0.1$ M

At t = 1 min, [A] = 0. 09 M

0. 09 = 0.1 – k

$\Rightarrow k = 0.01\ M\ min^{-1}$

At t = 2 min, $[A] = 0.1 - 0.01 \times 2$

= 0. 08 M, which is the value given.

$\therefore k = 0.01\ M\ min^{-1}$

Sol.13 For zero order reaction

$[A] = [A]_0 - kt$

We are given,

$k = 2 \times 10^{-2}\ mol\ L^{-1}sec^{-1}$

and at t = 25 sec, [A] = 0. 25 M

$[A]_0 = [A] + kt$

$= 0.25 + 2 \times 10^{-2} \times 25 = 0.75$ M

Sol.14 It is a zero order reaction (∵ unit of rate constant is $M\ sec^{-1}$)

$[H^+]_0 = \frac{6 \times 10^{-6}}{0.1 \times 10^{-3}} = 6 \times 10^{-2}$ M

$k = 10^7\ \text{mol L}^{-1}\ \text{sec}^{-1}$

time taken to disappear $= \dfrac{[H^+]}{k}$

$= \dfrac{6\times10^{-2}}{10^7}\ \text{sec} = 6 \times 10^{-9}\ \text{sec}$

Sol.15 Since it is a zero order reaction

$[A] = [A]_0 - kt$

When t = 1 hour, $[A] = \dfrac{1}{4}[A]_0$

($\because$ 75% reacted)

$\therefore \dfrac{1}{4}[A]_0 = [A]_0 - k$

$\Rightarrow k = \dfrac{3}{4}[A]_0\ \text{M hr}^{-1}$

When A is 10% unreacted,

$[A] = \dfrac{1}{10}[A_0]_0$

$\therefore \dfrac{1}{10}[A]_0 = [A]_0 - kt$

$\Rightarrow \dfrac{9}{10}[A]_0 = \dfrac{3}{4}[A]_0 t$

$\Rightarrow$t = 1. 2 hr

Sol.16 (i)We know, for first order reaction

$[A] = [A]_0 e^{-kt}$

$k = \dfrac{1}{t}\ln\dfrac{[A]_0}{[A]}$

At t = 72 min, 75% reaction completed, i. e. $[A] = \dfrac{1}{4}[A]_0$

$\therefore k = \dfrac{1}{72}\ln 4 = 0.019\ \text{min}^{-1}$

When reaction is 50% complete,

$t = t_{1/2} = \dfrac{\ln 2}{k} = 36\ \text{min}$

(ii)When reaction is 87. 5% complete, $[A] = 0.125[A]_0$,

$\therefore t = \dfrac{1}{k}\ln\dfrac{1}{0.125}$

t = 108 min

Sol.17 We have, for first order reaction

$k = \dfrac{1}{t}\ln\dfrac{[A]_0}{[A]_t}$

(i)At t = 10 min, reaction is 20% complete, i. e. $[A] = 0.8[A]_0$

$k = \dfrac{1}{10}\ln\dfrac{[A]_0}{0.8[A]_0}$

$k = 0.0223\ \text{min}^{-1}$

(ii)When reaction is 75% complete,

$[A] = \dfrac{1}{4}[A]_D$

$t = \dfrac{1}{k}\ln\dfrac{[A]_0}{[A]_t} = \dfrac{1}{0.0223}\ln\dfrac{[A]_0}{\frac{1}{4}.[A]_0}$

t = 62. 17 min.

Sol.18 Order will be equal to 1.

$t = \dfrac{1}{k}\ln\dfrac{[A]_0}{[A]_t}$

When reaction is 99. 9 % complete,

$[A]_t = 10^{-3}[A]_0$

$t_1 = \dfrac{1}{k}\ln\dfrac{[A]_0}{10^{-3}[A]_0} = \dfrac{3}{k}\ln 10 = \dfrac{6.909}{k}$

When reaction is 50% completed, $[A]_t = \dfrac{[A]_0}{2}$

$\therefore t_2 = \dfrac{1}{k}\ln\dfrac{[A]_0}{0.5[A]_0} = \dfrac{\ln 2}{k} = \dfrac{0.693}{k}$

We see that $t_2 \approx 10t_1$

Sol.19 We have, first order reaction

$N = N_0 e^{-kt}$

here, $k = 1.5 \times 10^{-3}\ \text{sec}^{-1}$

$N \propto 1.25$ (wt. $\propto$ molar)

$N \propto 5$

$\therefore 1.25 = 5e^{-1.5\times10^{-3}t}$

$\Rightarrow t = \dfrac{1}{1.5\times10^{-3}}\ln\dfrac{5}{1.25}$

t = 924. 3625

Sol.20 We have,

$[N]_0 = 500$

At t = 20 months, $[N]_t = 420$,

Using first order to rate law,

$k = \dfrac{1}{t}\ln\dfrac{[N]_0}{[N]_t}$

$k = 8.717 \times 10^{-3}\ \text{month}^{-1}$

The drug will be ineffective (will expire) when it has decomposed 30%, i. e. $[N] = 0.7[N]_0$.

$\therefore t = \dfrac{1}{t}\log\dfrac{[N]_0}{[N]_t} = \dfrac{1}{8.717\times10^{-3}}\log\dfrac{[N]_0}{0.7[N]_0}$

$t \approx 41$ months

Sol.21 For first order reaction

$k = \frac{1}{t}\log\frac{[A]_0}{[A]_1}$

We are given, 2% of virus gets inactivated every minute at the beginning, i. e. , at t = 1 min, $[A]_t = 0.98[A]_0$

$k = \frac{1}{1}\log\frac{[A]_0}{0.98[A]_0}$

$k = 0.02\ \text{min}^{-1}$

$k = 3.3 \times 10^{-4}\ \text{sec}^{-1}$.

Sol.22 If we assume the reaction to be of first order, then, let $[A]_t = \alpha$ and $[A]_0 = C_0$.

$a = C_0e^{-kt}$

At time

$t = 0, \alpha = C_0$

$t = t, \alpha = C_0e^{-k} = aC_0, a = e^{-k}$

$t = 2t, \alpha = C_0e^{-2k} = a^2C_0, a = e^{-k}$

$t = 3t, \alpha = C_0e^{-3k} = a^3C_0, a = e^{-k}$

Therefore, taking the reaction to be of first order, we found the concentration of A to be of the form given in question. Therefore, the reaction is of first order.

Sol.23 For first order reaction,

$[SO_2Cl_2] = [SO_2Cl_2]_0\ e^{-kt}$

$k = 2.2 \times 10^{-5}\ \text{sec}^{-1}$,

$t = 90$ min $= 5400$ sec

$\therefore \frac{[SO_2Cl_2]}{[SO_2Cl_2]_0} = e^{-5400\times2.2\times10^{-5}} = 0.888$

$\therefore$ 11. 2 % of $[SO_2Cl_2]$ decomposed.

Sol.24 For A, $k_1 = \frac{\ln2}{t_{1/2}} = \frac{\ln2}{5}$

Initial concentration = a_0 (let)

$[A]_t = a$

then,$a = e_0\,e^{-k_1t}$

For B, $k_2 = \frac{\ln2}{t_{1/2}} = \frac{\ln2}{1.5}$

Initial concentration

$[B]_0 = \frac{[A]_0}{4} = \frac{a_0}{4}$

$[B]_4 = b$

Then, $b = \frac{a_0}{4}e^{-k_2t}$

When a = b,

$a_0\,e^{-k_1t} = \frac{a_0}{4}e^{-k_2t}$

$4 = e^{(k_1-k_2)t}$

$\Rightarrow t = \frac{\ln4}{k_1-k_2}$

$= \frac{\ln4}{\frac{\ln2}{5}-\frac{\ln2}{15}} = \frac{2\ln2}{\ln2\left(\frac{1}{5}-\frac{1}{15}\right)} = \frac{2\times5\times15}{10}$

t = 15 min.

Sol.25 From the data, we observe that, when $[H_2]$ is halved, keeping [NO] constant, reaction rate gets halved. So, order w. r. t H_2 is 1.

When [NO] is doubled, keeping $[H_2]$ constant, reaction rate becomes 4 times so, order w. r. t. NO is 2.

Rate = $k[NO]^2[H_2]$

(a)Order = 2 + 1 = 3

(b)When, $[NO] = 1.5 \times 10^{-4}$ M,

$[H_2] = 4 \times 10^{-3}$ M,

Rate = 4.4×10^{-4} M sec^{-1}

$\therefore k = \frac{4.4\times10^{-4}}{(1.5\times10^{-4})^2\times(4\times10^{-3})^2}$

When $[NO] = 1.1 \times 10^{-3}$ M,

$[H_2] = 1.5 \times 10^{-3}$ M

(c)Rate = $4.88 \times 10^6 \times (1.1 \times 10^{-3})^2 \times (1.5 \times 10^{-3})$

Rate = 8.85×10^{-3} M sec^{-1}

Sol.26 From given data, we observe that, when $[Cl_2]$ is tripled, rate becomes 3 times, so, order w. r. t. Cl_2 is 1.

When [NO] is tripled, rate becomes 9 times, so, order w. r. t [NO] is 2.

(a)Order w. r. t. NO = 2

Cl = 1

(b)Rate = $k[NO]^2[Cl_2]$

(c)When $[Cl_2] = 0.05$ M, $[NO] = 0.05$ M,

Rate = 10^{-3}

$k = \frac{\text{rate}}{[NO]^2[Cl_2]} = \frac{10^{-3}}{(0.05)^2(0.05)} = 8\ M^{-2}\ \text{sec}^{-1}$

(d)If $[Cl_2] = 0.2$ M, $[NO] = 0.4$ M,

Rate = $k[NO]^2[Cl_2] = 8 \times (0.4)^2 (0.2)$

Rate = 0.256 mol sec^{-1} L^{-1}

Sol.27 Let us assume that this is first order reaction. i. e. $[A] = [A]_0 e^{-kt}$. Using this, we will calculate k at both times. If they are same, then our assumption is correct.

At t = 53 min, 50% reaction completed, i. e. $[A] = 0.5[A]_0$

$$\therefore k = \frac{\ln 2}{t} = \frac{0.693}{53} = 0.013 \text{ min}^{-1}$$

(i) We see that both values of k are same, this is first order reaction

(ii) $\frac{[N_2O]}{[N_2O]_0} = e^{-kt} = e^{-1.3\times10^{-2}\times100} = 0.27$

thus 73% of N_2O will decompose.

Sol.28 As in previous question, we assume order = 0 and calculate k at different time.

At t = 0 sec, $P = P_0 = 4 \times 10^3$ Pa

At t = 100 sec, $P = 3.5 \times 10^3$ Pa

We have, $k_1 = \frac{P_0 - P}{t} = \frac{(4-3.5)\times10^3}{100}$ Pa/s

$k_1 = 5$ Pa/s

At t = 200 sec, $P = 2 \times 10^3$ Pa

$$k = k_2 = \frac{(4-3)\times10^3}{200} = 5 \text{ Pa/s}$$

At t = 300 sec, $P = 2.5 \times 10^3$ Pa

$$k_3 = \frac{(4.2.5)\times10^3}{300} = 5 \text{ Pa}$$

We see that $k_1 = k_2 = k_3 = 5$ Pa/s is same for all. Hence this is zero order reaction, rate constant = 5 Pa/s

Sol.29 We know, for nth order reaction

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

We have, at $[A]_0$, $(t_{1/2})_1 = t = 50$ min

at $\frac{[A]_0}{2}$, $(t_{1/2})_2 = 25$ min

$$\therefore \frac{50}{25} = \left[\frac{\left(\frac{[A]_0}{2}\right)}{[A]_0}\right]^{n-1} = \frac{1}{2^{n-1}}$$

$$2 = \frac{1}{2^{n-1}} \Rightarrow 2^{n-1} = 2^{-1}$$

$n - 1 = -1$

$\Rightarrow n = 0$

Sol.30

	A	$\to$	B +	C
$t = 0$	P_0		0	0
t	$P_0 - x$		x	x
$t \to \infty$	0		P_0	P_0

We have, at time $t = t_1$

$P_1 = P_t = P_0 - x + x + x$

$P_2 = P_0 + x \Rightarrow x = P_2 - P_0$

at time, $t \to \infty$,

$P_t = P_3 = 2P_0$

$\Rightarrow P_0 = \frac{P_3}{2}$

Taking first order reaction,

$$k = \frac{1}{t}\ln\frac{(P_A)_0}{(P_A)_t} = \frac{1}{t}\ln\frac{P_0}{P_0 - x} = \frac{1}{t}\ln\frac{P_0}{P_0 - P_2 + P_0}$$

$$k = \frac{1}{t}\ln\frac{P_0}{2P_0 - P_2} = \frac{1}{3}\ln\frac{P_3}{2(P_3 - P_2)}$$

Sol.31 Here, we have, at time t

$P_B + P_C = P_2 = 2x \Rightarrow x = \frac{P_2}{2}$

at time $t \to \infty$, $P_B + P_0 = P_3 = 2P_0$

$\Rightarrow P_0 = \frac{P_3}{2}$

$$k = \frac{1}{t}\ln\frac{(P_A)_0}{(P_A)_t} = \frac{1}{t}\ln\frac{P_3}{\left(\frac{P_3}{2} - \frac{P_2}{2}\right)} = \frac{1}{t}\ln\frac{P_3}{P_3 - P_2}$$

Sol.32 $A \to B + C$

time			
t = 0	n_0	0	0
t	$n_0 - x$	x	x
$t \to \infty$	0	n_0	n_0

At time, t = 0, $V_r = V_1 = \frac{n_0 - a}{N}$

$\Rightarrow n_0 = \frac{NV_1}{a}$

(n-factor of A,B,C = a)

(using $NV_1 = n_0 a$)

Normality of reagent = N

At time, t = t,

$$V_n = V_2 = \frac{(n_0 - x)a + xa + xa}{N} = \frac{(n_0 + x)a}{N}$$

$\Rightarrow n_0 + x = \frac{NV_2}{a}$

$$x = \frac{NV_0}{a} - n_0 = \frac{N}{a}(V_2 - V_1)$$

$$k = \frac{1}{t}\ln\frac{n_0}{n_t} = \frac{1}{t}\ln\frac{n_0}{n_0 - x}$$

$$= \frac{1}{t}\ln\frac{NV_1}{a\left(\frac{NV_1}{a} - \frac{N}{a}\right)(V_2 - V_1)}$$

$$k = \frac{1}{t}\ln\frac{V_1}{2V_1 - V_2}$$

Sol.33 $A \to 2B + 3C$

time, t = 0 a

time, t $a - x$ $2x$ $3x$

time, $t \to \infty$ 0 $2a$ $3a$

Let n-factor of A, B and C be n and normality of reagent = N then at time, t

$N.\ V_2 = (a - x)n + 2xn + 3xn$

$NV_2 = n(a + 4x)$

$$a + 4x = \frac{NV_2}{n}$$

at time, $t \to \infty$

$NV_3 = 2a.\ n + 3a.\ n$

$\Rightarrow a = NV_3 = 5an$

$$a = \frac{NV_3}{5n}$$

$$\text{then} 4x = \frac{NV_2}{n} - \frac{NV_3}{5n}$$

$$x = \frac{N}{4n}\left(V_2 - \frac{V_3}{5}\right)$$

$$k = \frac{1}{t}\ln\frac{a}{a-x} = \frac{1}{t}\ln\frac{NV_3}{5n\left(\frac{NV_3}{5n} - \frac{NV_2}{4n} + \frac{NV_3}{20n}\right)}$$

$$= \frac{1}{t}\ln\frac{V_3}{V_3 - \frac{5}{4}V_2 + 4V_3} = \frac{1}{t}\ln\frac{4V_3}{5(V_3 - V_2)}$$

$$k = \frac{1}{t}\ln\frac{4}{5}\frac{V_3}{(V_3 - V_2)}$$

Sol.34 $S \to G + F$

time t = 0 a 0 0

time, t $a - x$ x x

time $t \to \infty$ 0 a a

Let specific rotation of Glucose and Fructose be θ_1 and θ_2 respectively

Then, at time t

$x\theta_1 + x\theta_2 = r_t$

$$x = \frac{r_t}{\theta_1 + \theta_2}$$

at time, $t \to \infty$

$a\theta_1 + a\theta_2 = r_\infty$

$$a = \frac{r_\infty}{\theta_1 + \theta_2}$$

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{1}{t}\log\frac{a}{a-x}$$

$$k = \frac{1}{t}\log\frac{r_\infty}{(\theta_1 + \theta_2)\left(\frac{r_\infty}{\theta_1 + \theta_2} - \frac{r_t}{\theta_1 + \theta_2}\right)}$$

$$k = \frac{1}{t}\log\frac{r_\infty}{r_\infty - r_1}$$

Sol.35 As $H_3(g) \to As(s) + \frac{3}{2}H_2(g)$

$t = 0 P_0$

$t = 1 P_0 - x \frac{3}{2} x$

Since, as a solid, it won't contribute to pressure.

$$\therefore \text{at time t, } P_t = P_0 - x + \frac{3}{2}x = P_0 + \frac{x}{2}$$

Lets assume reaction is first order and calculate k at different times, using $k = \frac{1}{4}\ln\frac{P_0}{P_0 - x}$

$t = 0$ $P_0 = 758 = P_t$

$t = 5$ hrs $P_t = 827 = P_0 + \frac{x}{2}$

$$827 = 8758 + \frac{x}{2}$$

$\Rightarrow x = 138$ mm

$$k = \frac{1}{5}\ \ln\ \frac{758}{758.138}$$

$k = 0.\ 04\ \text{hr}^{-1}$

$t = 7.\ 5$ hr $P_t = 856 = P_0 + \frac{x}{2}$

$$\Rightarrow \frac{x}{2} = 856 - 758$$

$x = 196$ mm

$$k = \frac{1}{7.5}\ln\frac{758}{758 - 196}$$

$k = 0.\ 039\ \text{hr}^{-1}$

$t = 10$ hr $P_t = 889 = P_0 + \frac{x}{2}$

$x = 2(883 - 758)$

$x = 248$ mm

$k = \frac{1}{10}\ln\frac{758}{758-248}$

$k = 0.039\ hr^{-1}$

Thus, all 3 values of k are approximately the same, hence first order reaction.

Sol.36 $(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$

time t = 0	P_0	0	0	0
time, t	$P_0 - x$	x	x	x
$t \rightarrow \infty$	0	P_0	P_0	P_0

Total pressure, at time t,

$P_t = P_0 - x + x + x + x \quad = P_0 + 2x$

Increase in pressure

$= (P_0 + 2x) - P_0 = 2x$

We will assume that this is a first order reaction and check the consistency of given data.

At t = 0, P_0 = 312 mm Hg

At t = 390 s, pressure increase ;

$\Delta P = 96$ mm Hg = 2x

x = 48 mm Hg

$\therefore k = \frac{1}{t}\ln\frac{P_0}{P_0 - x} \quad = \frac{1}{390}\ln\frac{312}{312-48}$

$k = 4.28 \times 10^{-4}$ s

At t = 1195 s, $\Delta P = 250 = 2x$

x = 125 mm Hg

$k = \frac{1}{1195}\mathit{ln}\frac{312}{312-125} \quad = 4.28 \times 10^{-4}$ s

At t = 3155 s,$\Delta P = 467 = 2x$

x = 233. 5 mm Hg

$k = \frac{1}{3155}\mathit{ln}\frac{312}{312-233.5} \quad = 4.30 \times 10^{-4}\ sec^{-1}$

At $t \rightarrow \infty, \Delta P = 2P_0 = 624$ mm Hg

$\approx$ 619 mm Hg

Thus, we see that all 3 values of k are approximately the same. Therefore, this is a first order reaction.

So, rate = $k[(CH_3)_2O]$, k

$= 4.28 \times 10^{-4}\ sec^{-1}$

Sol.37 $H_2O_2(g) \rightarrow H_2O(\ell) + \frac{1}{2}O_2(g)$

Here,$V_r \propto [H_2O_2]$

Assuming this is a first order reaction

$k = \frac{2.303}{t}\log\frac{[H_2O_2]_0}{[H_2O_2]_t} \quad = \frac{1}{t}\log\frac{V_0}{V_t}$

At time, t = 0, V_r 22. 8 cc = V_0

t = 10,V_r = 13. 3 cc = V_t

$k_1 = \frac{1}{10}\log\frac{22.8}{13.3} = 5.4 \times 10^{-2}\ min^{-1}$

t = 20,V_r = 8. 25 cc = V_t

$k_2 = \frac{1}{20}\log\frac{22.8}{8.25} = 5.1 \times 10^{-2}\ min^{-1}$

k_1 and k_2 are equal within experimental error. Therefore, first order reaction.

Sol.38 For inversion of cane sugar, assuming first order,

$k = \frac{1}{t}\log\frac{\theta_0 - \theta_\infty}{\theta_f - \theta_\infty}$

At time, t = 0, $\theta = \theta_0 = +13.1$

At time, $t \rightarrow \infty, \theta = \theta_\infty = -3.8$

At time, t = 60, $\theta_+ = 11.6^\circ$

Sol.39 $A(g) \rightarrow 2B(g) + C(g)$

time, t = 0	P_0	0	0
time, t	$P_0 - x$	2x	x
time,$t \rightarrow \infty$	0	$2P_0$	P_0

At, $t \rightarrow \infty, P_t = 3P_0 = 270$ mm Hg

P_0 = 90 mm Hg = (P_A)

At, t = 10 min,$P_t = P_0 - x + 2x + x$

$= P_0 + 2x = 176$

2x = 176 – 90

x = 43 mm Hg

$(P_A)_+ = P_0 - x \ = 90 - 43 \ = 47$ mm Hg

Now, since, this is first order reaction.

$k = \frac{2.303}{t}\log\frac{(P_A)_0}{(P_A)_+} \quad = \frac{2.303}{10}\log\frac{90}{47}$

$k = 6.49 \times 10^{-2}\ min^{-1}$

$k_1 = .\frac{1}{60}2.303\mathit{log}\frac{13.1-(-3.8)}{11.6-(-3.8)}.$

$= 1.55 \times 10^{-3}\ min^{-1}$

At time, t = 120 min, $\theta_t = +10.2^\circ$

$k_2 = \frac{2.303}{120}\log\frac{(13.1)-(-3.8)}{(10.2)-(-3.8)}$

$= 1.57 \times 10^{-3}\ min^{-1}$

At time, t = 180 min, $\theta_t = +9.0^\circ$

$k_3 = \frac{2.303}{180}\log\frac{(13.1)-(-3.8)}{(9.0)-(-3.8)} = 1.54 \times 10^{-3}\ min^{-1}$

At time, t = 360 min, $\theta_t = +5.87^\circ$

$k_4 = \frac{2.303}{360}\log\frac{(13.1)-(-3.8)}{(5.87)-(-3.8)} = 1.55 \times 10^{-3}\ min^{-1}$

We see that, k_1, k_2, k_3 and k_4 are all same within experiment value.

Therefore, this is a first order reaction

Half-life = $\frac{0.693}{k} = \frac{0.693}{6.49 \times 10^{-2}} = 10.677$ min

(i) $(P_A)_I$ = 90 mm Hg

(ii) $(P_A)_f$ = 47 mm Hg

(iii) k = 6. 49 × 10^{-2} min^{-1}

(iv) $t_{1/2}$ = 10. 67 min

Sol.40 $2N_2O_5(g)\rightarrow 4NO_2(g)+O_2(g)$

time, t = 0 $\quad P_0 \quad 0 \quad 0$

time, t = t $\quad P_0 - 2x \quad 4x \quad x$

$t\rightarrow\infty \quad 0 \quad 2P_0 \quad \dfrac{P_0}{2}$

At $t\rightarrow\infty$, P_t = 584. 5 = $2P_0 + \dfrac{P_0}{2}$

$\Rightarrow \dfrac{5P_0}{2}$ = 584. 5

$\Rightarrow P_0$ = 233. 8 mm Hg

At t = 30 min,

P_t = 284. 5 = $P_0 - 2x + 4x + x$

$\Rightarrow P_0 + 3x$ = 284. 5

3x = 284. 5 – 233. 8

x = 16. 9 mm Hg

$P_{N_2O_5} = P_0 - 2x$

= 233. 8 – 2 × 16. 9 = 200 mm Hg

We have,

$$\frac{-1}{2}\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

$$\int_{[N_2O_5]_0}^{[N_2O_5]_t}\frac{d[N_2O_5]}{[N_2O_5]_0} = -2k\int_0^t dt$$

$$\ln\frac{[N_2O_5]_t}{[N_2O_5]_0} = -2kt$$

$$k = \frac{2.303}{2t}\log\frac{[N_2O_5]_0}{[N_2O_5]_t}$$

$$k = \frac{2.303}{2t}\log\frac{(P_{N_2O_5})_0}{(P_{N_2O_5})_t} \qquad (\because P_{N_2O_5}\propto[N_2O_5])$$

$$= \frac{2.303}{2\times30}\log\frac{233.8}{200}$$

k = 2. 605 × 10^{-3} min^{-1}.

Sol.41 (a)Assuming first order reaction

$$k = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

We have, V_0 = 22. 8 cc

At t = 10 min, V_t = 13. 8 cc

$$k_1 = \frac{2.303}{10}\log\frac{22.8}{13.8} = 5.02\times10^{-2}\ \text{min}^{-1}$$

At t = 20 min, V_t = 8. 25 cc

$$k_2 = \frac{2.303}{20}\log\frac{22.8}{8.25} = 5.08\times10^{-2}\ \text{min}^{-1}$$

Since, $k_1 \approx k_2$. This is first order reaction.

(b)$t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{5.05\times10^{-2}}$ = 13. 75 min

(c)At t = 25 min,

$$k = \frac{2.303}{25}\log\frac{V_0}{V_t}$$

Fraction decomposed

$$1.\ \frac{V_t}{V_0} = 1.\ 10\ \frac{-25\times5.05\times10^{-2}}{2.303} = 1 - 0.\ 284$$

Fraction decomposed = 0. 716

Sol.42 $H_2O_2 \rightarrow H_2O + \dfrac{1}{2}O_2$

We are given complete dissociation gives 46. 34 mL O_2.

Also $V_{O_2} \propto [H_2O_2]$

(V_{O_2} is volume of O_2 a given sample of H_2O_2 can given)

$\therefore [H_2O_2]_0 \propto$ 46. 34

Also, at t = 5.1 days, V_{O_2} = 10. 31 mL

then $[H_2O_2]_t \propto$ (46. 34 –10. 31)

So, $\quad k = \dfrac{2.303}{t}\log\dfrac{[H_2O_2]_0}{[H_2O_2]_t}$

$$k = \frac{2.303}{5.1}\log\frac{46.34}{46.34-10.31}$$

k = 4. 93 × 10^{-2} days^{-1}.

When 20 mL ,O_2 lost,

$[H_2O_2]_t \propto$ (46. 34 –20. 00)

$$t = \frac{2.303}{k}\log\frac{[H_2O_2]_0}{[H_2O_2]_0-[H_2O_2]_t}$$

$$= \frac{2.303}{4.93\times10^{-2}}\log\frac{46.34}{46.34-20}$$

t = 11. 45 days

Sol.43 A(aq) → B(aq) + C(aq)

t = 0 $\quad n_0$

t = t $\quad n_0 - x \quad x \quad x$

$t\rightarrow\infty \quad 0 \quad n_0 \quad n_0$

At $t\rightarrow\infty, \theta_\infty$ = –5° = $n_0.\ \theta_B + n_0\theta_C$

We have, θ_A = 20°, θ_B = 30°,

θ_C = –40°

$\therefore 30n_0 - 40n_0 = -5$

n_0 = 0. 5

At time, t = 6. 43 min.

$\theta_t = (n_0 - x)\theta_A + x(\theta_B + \theta_C)$ = 2. 5

$20n_0$ + x(30. 40 – 20) = 2. 5

$30x = 20 \times 0.5 - 2.5$

$30x = 7.5$

$x = 0.25$

For first order conversion,

$$k = \frac{2.303}{t}\log\frac{n_0}{n_0 - x}$$

$$= \frac{2.303}{6.93}\log\frac{0.5}{0.5 - 0.25}$$

$k = 0.1\ \text{min}^{-1}$

Sol.44

$$x \begin{array}{l} \nearrow^{k_1}\ B \\ \searrow_{k_2}\ C \end{array} \quad (B = y,\ C = z)$$

We have,

$$\frac{d[x]}{dt} = -(k_1 + k_2)[x]$$

$$\int_{[x]_0}^{[x]_t} \frac{d[x]}{[x]} = -(k_1 + k_2)\int_0^t dt$$

$\Rightarrow [x]_t = [x]_0 e^{-kt}$, $k = k_1 + k_2$

Now, $\dfrac{d[B]}{dt} = k_1[x]_t$

$$\frac{d[B]}{dt} = k_1[x]_0 e^{-kt}$$

$$\int_0^{[B]_t} d[B] = k_1[x]_0 \int_0^t e^{-kt}$$

$$[B]_t = \frac{-k_1[x]_0}{k} e^{-kt}\Big|_0^t$$

$$[B]_t = \frac{-k_1[x]_0}{k_1 + k_2}(1 - e^{-kt})$$

Similarly $[C]_t = \dfrac{k_2[x]_0}{k_1 + k_2}(1 - e^{-kt})$

$[B]_t + [C]_t = [y] + [x]$

$$= \frac{k_1[x]_0}{k}(1 - e^{-kt}) + \frac{k_2[x]_0}{k}(1 - e^{-kt})$$

$$= \left(\frac{k_1 + k_2}{k}\right)[x]_0(1 - e^{-kt}) = [x]_0\ e^{(1 - e^{-kt})}$$

$$\therefore \frac{[x]_t}{[y] + [2]} = \frac{e^{-kt}}{1 - e^{-kt}} = \frac{1}{e^{+(k_1 + k_2)t} - 1}$$

Sol.45 Using results of previous question

$[C]_t = \dfrac{k_2[A]_0}{k}(1 - e^{-kt})$, $k = k_1 + k_2$

$[A]_t = [A]_0 e^{-kt}$

$$\frac{[C]_t}{[A]_t} = \frac{k_2}{k_1 + k_2}\frac{(1 - e^{-kt})}{e^{-kt}}$$

$$= \frac{1}{1 + \frac{k_1}{k_2}}(e^{-kt} - 1)$$

We have, $k_1 = x\ \text{hr}^{-1}$, $k_2 = 10\, k_1$

$= 10 \times \text{hr}^{-1}$, $t = 1$ hr

$$\therefore \frac{[C]_t}{[A]_t} = \frac{1}{1 + \frac{1}{10}}(e^{(x + 10x)} - 1)$$

$$\frac{[C]_t}{[A]_t} = \frac{10}{11}(e^{11x} - 1)$$

Sol.46 We have,

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$,

$k_1 = \dfrac{\ln 2}{\ln 1}$, $k_2 = \dfrac{\ln 2}{2}$

For [A]

$$\frac{d[A]}{dt} = -k_1[A]$$

$\Rightarrow [A] = [A]_0 e^{-k_1 t}$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$

$$\frac{d[B]}{dt} + k_2[B] - k_1[A]_0\ e^{-k_1 t} = 0 \ldots \text{(i)}$$

This is a linear differential equation.

Solving this, we get

$$[B]_t = \frac{k_1[A]_0}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}]$$

Now, at $[B]_{\text{max}}$, $\dfrac{d[B]_t}{dt} = 0$

In (i), putting $\dfrac{d[B]_t}{dt} = 0$, we get

$k_1[A]_0\ e^{-k_1 t} = k_2[B]$

$$k_1[A]_0 e^{-k_1 t} = \frac{k_2 k_1[A]_0}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}]$$

$$k_2 e^{-k_1 t}.k_1 e^{-k_1 t} = k_2 e^{-k_1 t}.k_2 e^{-k_2 t}$$

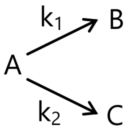
$$\frac{k_1}{k_2} = e^{(k_1 - k_2)t}$$

$$t = \left(\frac{\log k_1 - \log k_2}{k_1 - k_2}\right).2.303$$

$$t = \frac{1}{k_1 - k_2}\ln\frac{\ln 2}{4.\ln 2} = \frac{-4}{\ln 2}\ln\frac{1}{2} = 4$$

$\therefore t = 4$ min.

Sol.47



From 0, 4s, $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

We need, $\frac{[B]}{[C]} = 2 = \frac{k_1}{k_2}$

Let temperature be T.

By Arrhenius equation.

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

For A $\xrightarrow{k_1}$ B, $k_2 = k_1$, $k_1 = 8$,

$E_a = 20$ kJ/mol (E_1), $T_1 = 300$, $T_2 = T$

$$\log\frac{k_1}{8} = \frac{(E_a)_1}{2.303R}\left(\frac{1}{300} - \frac{1}{T}\right)$$

$$k_1 = 8 \text{ antilog}\left[\frac{(E_a)_1}{2.303R}\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

For A $\xrightarrow{k_2}$ C, similarly,

$$k_2 = 2 \text{ antilog}\left[\frac{(E_a)_2}{2.303R}\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

$$\frac{k_1}{k_2} = 2$$

$$4\text{antilog}\left[\frac{((E_a)_1 - (E_a)_2)}{2.303R}\right]\left(\frac{1}{300} - \frac{1}{T}\right) = 2$$

$$\frac{(E_a)_1.(E_a)_2}{2.303R}\left(\frac{1}{300} - \frac{1}{T}\right) = \log\frac{1}{2}$$

$(E_a)_1 = 20$ kJ/mol,

$(E_a)_2 = 2.\ 8314$ kJ/mol

$$\Rightarrow \frac{(28.314 - 20)\times 10^3}{8.314}\left(\frac{1}{300} - \frac{1}{T}\right) = 0.\ 7$$

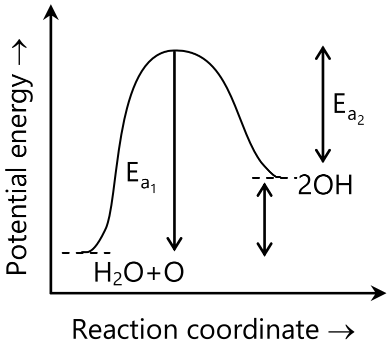
$$\frac{1}{300} - \frac{1}{T} = 7 \times 10^{-4}$$

$$\frac{1}{T} = 2.\ 63 \times 10^{-3}$$

T = 379. 75 K

Sol.48 $H_2O + O \rightarrow 2OH^-, E_{a_1}$

$2OH^- \rightarrow H_2O + O, E_{a_2}$



$E_{a_2} = E_{a_1} - \Delta H$

= (77. 72) kJ mol^{-1}

$E_{a_2} = 5$ kJ mol^{-1}

Sol.49 For $t_{1/2} = 1$ min, $k = \frac{0.693}{t_{1/2}}$

$= 0.\ 693 \text{ min}^{-1} = 1.\ 155 \times 10^{-2}\text{s}$

Now, $k = Ae^{\frac{-E_a}{RT}} \Rightarrow T = \frac{E_a}{R}\left(\ln\frac{A}{k}\right)^{-1}$

$A = 5 \times 10^{13}$ sec^{-1}

$E_a = 104.\ 5$ kJmol^{-1}

$$T = \frac{104.5\times 10^3}{8.134}\left(\ln\frac{5\times 10^{13}}{1.155\times 10^{-2}}\right)^{-1}$$

T = 349. 1 K

Sol.50 From Arrhenius equation

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

For $T_1 = 27°C = 300$ K and

$T_2 = 47°C = 320$ K, $\frac{k_2}{k_1} = 4$

$$\therefore \log 4 = \frac{E_a}{2.303\times 8.314}\left(\frac{1}{300} - \frac{1}{320}\right)$$

$$E_a = \frac{\log 4\times 2.303\times 8.314\times 300\times 320}{20}$$

$E_a = 55.\ 33$ kJ/mol

Sol.51 For $t_{1/2} = 2$ hr, $k = \frac{0.693}{t_{1/2}}$

$= \frac{0.693}{2}\text{hr}^{-1}$

$= 9.\ 625 \times 10^{-5}$ sec^{-1}

So, we have, $k_1 = 3.\ 46 \times 10^{-5}$ sec^{-1}

$k_2 = 9.\ 625 \times 10^{-5}$ sec^{-1}

$E_a = 100$ kJ mol^{-1}

$T_1 = 25°C = 298$ K

$T_2 = T$

By Arrhenius equation.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\log \frac{9.625\times10^{-5}}{3.46\times10^{-5}} = \frac{100\times10^{3}}{2.303\times8.314}\left(\frac{1}{298}-\frac{1}{T}\right)$$

$$\Rightarrow \frac{1}{298}-\frac{1}{T} = 8.5\times10^{-5}$$

$$\Rightarrow \quad T = 306\ K$$

Sol.52 By Arrhenius equation

$$k = A e^{-E_a/RT}$$

$$\frac{k_2}{k_1} = e^{(E_{a_1}-E_{a_2})/RT}$$

We have,

$E_{a_1} = 75\ kJ\ mol^{-1}$

$E_{a_2} = 25\ kJ\ mol^{-1}$

$T = 25^\circ C = 298\ K$

$$\therefore \frac{k_2}{k_1} = 5.8\times10^{8}$$

Therefore, rate of reaction increases by 5.8×10^{8} times.

Sol.53 Temperature coefficient

$$= \frac{k_{308k}}{k_{298k}} = 1.75$$

By Arrhenius equation

$$\log\frac{k_{308k}}{k_{298k}} = \frac{E_a}{2.303k}\left(\frac{1}{298}-\frac{1}{308}\right)$$

$$E_a = \frac{\log 1.75\times2.303\times8.314\times298\times308}{10}$$

$= 42.711\ kJ\ mol^{-1}$

$E_a = 10.757\ kJ\ mol^{-1}$

Sol.54 At $T_1 = 380^\circ C = 653\ K$,

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{360}$$

$= 1.925\times10^{-3}\ min^{-1}$

$T_2 = 450^\circ\ C = 723\ K,\ k_2 = k$

$E_a = 200\ k\ J\ mol^{-1}$

By Arrhenius equation

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\log \frac{k}{1.925\times10^{-3}} = \frac{200\times10^{3}}{2.303\times8.314}\left(\frac{1}{653}-\frac{1}{723}\right)$$

$$\log \frac{k}{1.925\times10^{-3}} = 1.548$$

$k = 6.81\times10^{-2}\ min^{-1}$

Time required for 75 % reaction

$$= 2t_{1/2} = \frac{2\times693}{6.8\times10^{-2}}$$

time= 20. 4 minutes

Sol.55 We have,

$k_1 = 10^{12}\ e^{-81.28\times10^3/RT}$

$k_2 = 10^{11}\ e^{-43.1\times10^3/RT}$

$k_1 = k_2$, when

$$10^{12}\ e^{\frac{-81.28\times10^3}{8.3\times T}} = 10^{11}\ e^{\frac{-43.1\times10^3}{8.3\times T}}$$

$$e^{\frac{(81.28-43.1)\times10^3}{8.3\times T}} = 10$$

$$\frac{38.18\times10^3}{8.3\times T} = \ell n\ 10 = 2.3$$

$$T = \frac{38.18\times10^3}{2.3\times8.3}$$

$T = 2000\ K$

Sol.56 We have,

(i) $NO + Br_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NOBr_2$

(ii) $NOBr_2 + NO \xrightarrow{k_3} 2NOBr$

This is RDS

Here, we use equilibrium approach, as equilibrium is achieved fast

Rate = $k_3[NOBr_2]\ [NO]$

For equilibrium of (i),

$$\frac{k_1}{k_2} = \frac{[NOBr_2]}{[NO][Br_2]}$$

$$[NOBr_2] = \frac{k_1}{k_2}[NO]\ [Br]$$

$$\text{Hence, rate} = \frac{k_1k_3}{k_2}[NO]\ ^2[Br] = k[NO]\ ^2[Br_2]$$

$$k = \frac{k_1k_3}{k_2}$$

Sol.57 (i) $2NO \rightarrow N_2O_2$

equilibrium constant = k_1 (fast)

(ii) $N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$

RDS

(iii) $N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$

As equilibrium step is fast, we use equilibrium approach

EXERCISE – II JEE ADVANCED

from (i), $k_1 = \frac{[N_2O_2]}{[NO]^2}$

$[N_2O_2] = k_1[NO]^2$

Also, from (ii), Rate = $k_2[N_2O_2][H_2]$

$= k_1k_2[NO]^2[H_2]$

$= k[NO]^2[H_2]$

$k = k_2k_3$

Sol.59 (i) $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ [fast]

(ii) $N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (RDS)

from equilibrium of (i),

$\frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2}$

$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$

from (ii)

Rate = $\frac{1}{2}\frac{d[NO_2]}{dt} = k_2[O_2][N_2O_2]$

$= \frac{k_2k_1}{k_{-1}}[NO]^2[O_2]$

Rate = $\frac{1}{2}\frac{d[NO_2]}{dt} = k[NO]^2[O_2]$,

$k = \frac{k_2k_1}{k_{-1}}$

Sol.60 (a) $H_2 + I_2 \rightarrow 2HI$

since, this is one step, rate = $k[H_2][I_2]$

(b) (i) $I_2 \rightarrow 2I$

equilibrium constant = k_1, fast

(ii) $2I + H_2 \xrightarrow{k_2} 2HI$, RDS

from (i) equilibrium, $k_1 = \frac{[I]^2}{[I_2]}$

$[I]^2 = k_1[I_2]$

from (ii)Rate = $k_2[I]^2[H_2]$

$= k_2k_1[I_2][H_2]$

$= k[H_2][I_2]$, $k = k_2k_1$

(c) (i) $I_2 \rightarrow 2I$

equilibrium constant = k_1, fast

(ii) $I + H_2 \rightarrow HI_2$

(iii) $IH_2 + I \xrightarrow{k_3} 2HI$, RDS

equilibrium constant = k_2, fast

from equilibrium (i), $k_1 = \frac{[I]^2}{[I_2]}$

$[I]^2 = k_1[I_2]$

from equilibrium (ii),

$k_2 = [HI]^2 \frac{[IH_2]}{[I][H_2]}$

$[IH_2] = k_2[I][H_2]$

since (iii) is RDS,

Rate = $k_3[IH_2][I]$

$= k_3k_2[I]^2[H_2]$

$= k_1k_2k_3[I_2][H_2]$

Rate = $k[H_2][I_2]$

(d) No, it cannot distinguish between the three mechanisms as all the 3 molecules gives the same rate law.

(e)Mechanism (a) becomes most improbable as it just involves one step and it is highly unlikely that I_2 and H_2 will combine directly at 200°C without breaking into radicals.

Sol.1 [B] We know,

Coefficient in rate law

$= \frac{1}{\text{stiochiometric coefficient}}$

Given rate law

$+\frac{1}{2}\frac{d[C]}{dt} = \frac{-1}{3}\frac{d[D]}{dt} = \frac{+1}{3}\frac{d[A]}{dt}$

$= -\frac{d[B]}{dt}$

Reaction is

$3D + B \rightarrow 2C + 4A$

Sol.2 [D] If volume is reduced to half, pressure will get doubled.

Now, reaction is first order w. r. t O_2 and second order w. r. t N_2

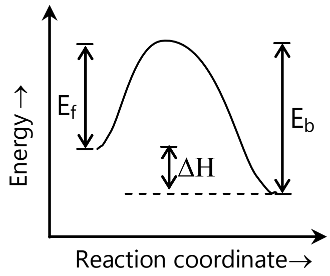
$\therefore$ rate = $k[O_2][N_2]^2$

$r_f = k[2O_2][2N_2]^2$

$r_f = k[2O_2][2N_2]^2$

$= 8r_i$

Sol.3 [C] We have



$\therefore |\Delta H| = E_b - E_f$

$= (200 - 180)\ \text{kJ mol}^{-1}$

$|\Delta H| = 20\ \text{kJ/mol}$

Sol.4 [D] For zero order reaction

rate, $\frac{d[B]}{dt} = k$

$[B] = kt$

$[A] = [A]_0 - kt$

At time $t = t_{3/4}$, $[A] = \frac{1}{4}[A_0]$

$\Rightarrow t = \frac{3[A]_0}{4k}$

$\Rightarrow t_{3/4} \propto [A_0]$

Similarly, $t_{1/2} \propto [A_0]$

Sol.5 [C] Here, $t_{1/2} \propto [A]_0$, therefore, it is a zero order reaction.

So, rate of reaction $\left(\frac{d[A]}{dt}\right)$ will be independent of time.

Sol.6 [B] The given option is correct as there is very little probability for more than 3 atoms to collide simultaneously.

Sol.7 [C] We have

$k = \frac{2.303}{t}\log\frac{a_0}{a_0 - x}$

$kt = 2.303 \log a_0 - 2.30 \log(a_0 - x)$

$\log(a_0 - x) = \frac{-kt}{2.303} + \log a_0$

Slope of log $(a_0 - x)$ vs.

+ graph $= \frac{-kt}{2.303}$

Slope of given graph $= -3.3 \times 10^{-3} = \frac{-k}{2.303}$

$\Rightarrow k = 7.7 \times 10^{-3}$

Sol.8 [C] As shown in QS of exercise I.

Volume strength $= 5.6\ N_0 = 16.8^\circ$

Now, after 2. 303 hours, let normality be N.

When 20 mL of this solution is diluted, Normality becomes

$\frac{N.20}{100} = \frac{N}{5}$

It is diluted against 0. 02 M $KMnO_4$.

Under acidic conditions, normality of $KMnO_4$ = M × 5

$= 0.02 \times 5 = 0.1$ N

Now, using $N_1V_1 = N_2V_2$

$\frac{N}{5}.\ 25 = 0.1 \times 37.5$

N = 0. 75 N

Now. volume strength

$V = N \times 5.6$

$= 0.75 \times 5.6 = 4.2$ V

Now,

$k = \frac{2.303}{t}\log\frac{V_0}{V_t}$

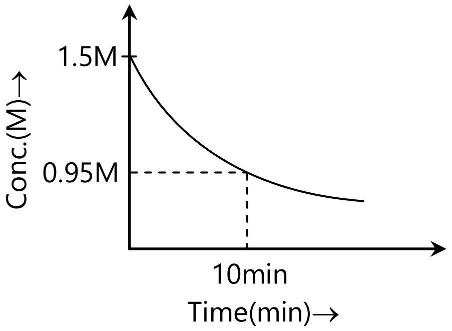
$t = 2.303$ hours, $V_0 = 16.8$ V,

$V_f = 4.2$ V

$k = \frac{2.303}{2.303}\log\frac{16.8}{4.2}$

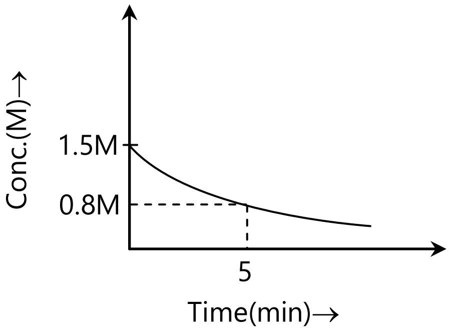
$k = 0.60\ \text{hr}^{-1}$

Sol.9 [A] For experiment 1,



Average rate $= \frac{-\Delta[A]}{\Delta t} = \frac{0.55}{10} = 0.055\ \text{min}^{-1}$

For experiment 2,



Average rate, $r_2 = \frac{\Delta A}{\Delta t}$

$= \frac{0.2}{5}\text{ M min}^{-1} = \frac{1}{25}\text{ M min}^{-1}$

$\Rightarrow \frac{r_1}{r_2} = \frac{0.55}{1/25} = 1.375 \approx 1.5 = \frac{[A]_{0_1}}{[A]_{0_2}}$

Hence the reaction is first order

When [A] = 1. 8 M

Rate, r = 1. 8 × [x] 2

$= \frac{1.8}{25}\text{ M min}^{-1} = 0.072\text{ M min}^{-1}$

$\approx 0.08\text{ M min}^{-1}$

Sol.10 [A] Since $k_1 << k_2$ second reaction will have the most activation energy

Further, since the overall reaction is exothermic, therefore the final energy of products should be less than the reactants plot which satisfies above 2 is (A).

Sol.11 [A] $NO(g) + Br_2(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NOBr_2(g)$

$NOBr_2(g) + NO(g) \xrightarrow{k_3} 2NOBr(g)$

We use equilibrium approach

Since second step is RDS,

Rate, R = $-k_3[NOBr_2]\,[NO]$

From equilibrium of (i),

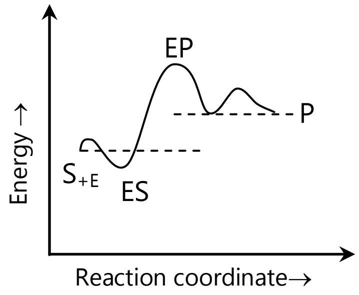
$\frac{k_1}{k_2} = \frac{[NOBr_2]}{[NO][Br_2]}$

$\Rightarrow [NOBr_2] = \frac{k_1}{k_2}[NO]\,[Br_2]$

Therefore, rate = $\frac{k_3k_1}{k_2}[NO]^2[Br_2]$

Order w. r. t. NO = 2

Sol.12 [B]



This is the plot for enzyme catalysed reaction.

Correct option is (B).

Sol.13 [A, D] We have, emission rate of SO_3

$= 6.93 \times 10^{-6}$ gm/L/day

$= \frac{6.93\times10^{-6}}{80}$ mol/L/day

$= 8.6625 \times 10^{-8}$ mol/L/day

For decomposition of SO_3,

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3}\text{ day}^{-1}$

$\frac{d[SO_3]}{dt} = 8.6625 \times 10^{-8}$

$- 693\times10^{-3}[SO_3]$

At steady state, $\frac{d[SO_3]}{dt} = 0$

$\Rightarrow [SO_3] = \frac{8.6625\times10^{-8}}{6.93\times10^{-3}}$

$[SO_3] = 1.25 \times 10^{-5}$ M

In 10^{-3} of air, moles of SO_3

$= 1.25 \times 10^{-5}\times10^{3}$

$= 1.25\times10^{-2}$ mol

When dissolved in water (1 L),

$[SO_3] = 1.25 \times 10^{-2}$ M

Normality of SO_3 = 2M

$= 2.5 \times 10^{-2}$ N

$N_1V_1 = N_2V_2$

$2.5 \times 10^{-2} \times 1000 = 1 \times V_2$

V_2 = 25 mL

$SO_3 + H_2O \rightarrow H_2SO_2$

Rate of H_2SO_4 production

$= 980\text{ kg/day} = \frac{980\times10^3}{98}$ mol/day

$= 10^9$ mol/day

SO_3 required = H_2SO_4 manufactured = 10^4 mol/day

Now, $V = \frac{\text{number of moles}}{M}$

$= \frac{10^4}{1.25\times10^{-5}} = 8 \times 10^8$ L/day

If SO_3 emission stopped,

$\frac{d[SO]_3}{dt} = -6.93 \times 10^{-3}[SO_3]$

$\Rightarrow [SO_3] = [SO_3]_0\, e^{-6.93\times10^{-3}t}$

$[SO_3]_0 = [SO_3]_0\, e^{-6.93\times10^{-3}t}$

$[SO_3]_0 = 1.25 \times 10^{-5}$ M

t = 1000 days

$\therefore [SO_3]_0 \approx 1.2 \times 10^{-8}$ M

Sol.14 [A, B, D]

$\frac{-d[A]}{dt} = k[A]^{1/2}$

$$\int_{[A]_0}^{[A]} \frac{-d[A]}{[A]^{1/2}} = \int_0^t k\,dt$$

$$2[A]^{1/2}\Big|_{[A]_0}^{[A]} = kt\Big|_0^t$$

$$[A]^{\,1/2} = [A]_0^{1/2} = \frac{kt}{2}$$

$$k = \frac{-1}{2}(A_0^{1/2}.A^{1/2)}$$

$$\sqrt{A} = \frac{kt}{2} + \sqrt{A_0}$$

Straight line

At t = $t_{1/2}$, $[A] = \frac{[A]_0}{2}$

$$t_{1/2} = \frac{2\sqrt{2}k}{[A_0]^{1/2} - \frac{[A_0]_0^{1/2}}{\sqrt{2}}}$$

$$\frac{2\left([A_0]_0^{1/2}\,2([2A]_0^{1/2} - \frac{[A]}{\sqrt{2}}\right)^{1/2}}{k}$$

$$= \frac{2\sqrt{2}k}{(\sqrt{2}-1)[A]_0} = \frac{2[A]_0^{1/2}}{k}(\sqrt{2}-1)$$

At t = $t_{3/4}$, $[A] = \frac{[A]_0}{4}$

$$\therefore t_{3/4} = \frac{2k}{[A]_0^{1/2} - \frac{[A]_0^{1/2}}{2}}$$

$$\frac{2\left([A]_0^{1/2} - \frac{[A]_0^{1/2}}{2}\right)}{k}$$

$$t_{3/4} = \frac{\sqrt{[A]_0}}{k}$$

Sol.15 [A, D] $H_2O_2(g) \rightarrow H_2O(\ell) + \frac{1}{2}O_2(g)$

Here, $V_r \propto [H_2O_2]$

Assuming this is a first order reaction

$$k = \frac{2.303}{t}\log\frac{[H_2O_2]_0}{[H_2O_2]_t} = \frac{1}{t}\log\frac{V_0}{V_t}$$

At time, t = 0, V_r 22.8 cc = V_0

t = 10, V_r = 13.3 cc = V_t

$$k_1 = \frac{1}{10}\log\frac{22.8}{13.3} = 5.4 \times 10^{-2}\ \text{min}^{-1}$$

t = 20, V_r = 8.25 cc = V_t

$$k_2 = \frac{1}{20}\log\frac{22.8}{8.25} = 5.1 \times 10^{-2}\ \text{min}^{-1}$$

k_1 and k_2 are equal within experimental error. Therefore, first order reaction.

Sol.16 [C, D]

(A) is correct

Rate, R = $k[A]^m[B]^n[C]^0$

log R = log k + m log[A] + n log[B]

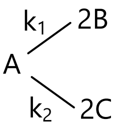
If all concentration other than [A] are constant,

Then $\frac{d(\log k)}{d(\log[A])} = m$

(C)Order of reaction can be fractional

(D) Order of a reaction can only be determined experimentally

Sol.17 [C] Order of an elementary reaction cannot be fractional, through the overall order of a reaction can be fractional.



We have, $\frac{[B]}{[C]} = \frac{k_1}{k_2} = \frac{1}{2}$

For every mole of A consumed, $\frac{1}{3}$ mole used for forming B and rest for forming C.

$[A]_0$ = 2 moles

At end of 50% reaction, A_0 = 1 mole

$B_n = \frac{1}{3} \times 2 \times 1 = \frac{2}{3}$ moles

$C_n = \frac{2}{3} \times 2 \times 1 = \frac{4}{3}$ moles

[Since, for every mole A, 2 moles of B (or C) is produced]

Sol.18 [D] A(aq) → B(aq) + C(aq)

t = 0 n_0

t = t $n_0 - x$ x x

t →∞ 0 n_0 n_0

At t → ∞, $\theta_\infty = -5^\circ = n_0.\theta_B + n_0\theta_C$

We have, $\theta_A = 20^\circ$, $\theta_B = 30^\circ$,

$\theta_C = -40^\circ$

$\therefore 30n_0 - 40n_0 = -5$

$n_0 = 0.5$

At time, t = 6.43 min.

$\theta_t = (n_0 - x)\theta_A + x(\theta_B + \theta_C) = 2.5$

$20n_0 + x(30.40 - 20) = 2.5$

$30x = 20 \times 0.5 - 2.5$

$30x = 7.5$

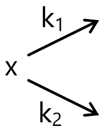
$x = 0.25$

For first order conversion,

$$k = \frac{2.303}{t}\log\frac{n_0}{n_0 - x} = \frac{2.303}{6.93}\log\frac{0.5}{0.5 - 0.25}$$

$k = 0.1\ \text{min}^{-1}$

Sol.19 [A]



(B = y, C = z)

We have,

$$\frac{d[x]}{dt} = -(k_1 + k_2)[x]$$

$$\int_{[x]_0}^{[x]_t}\frac{d[x]}{[x]} = -(k_1 + k_2)\int_0^t dt$$

$\Rightarrow [x]_t = [x]_0e^{-kt},\ k = k_1 + k_2$

Now, $\frac{d[B]}{dt} = k_1[x]_t$

$$\frac{d[B]}{dt} = k_1[x]_0e^{-kt}$$

$$\int_0^{[B]_t} d[B] = k_1[x]_0\int_0^t e^{-kt}$$

$$[B]_t = \frac{-k_1[x]_0}{k}e^{-kt}\Big|_0^t$$

$$[B]_t = \frac{-k_1[x]_0}{k_1 + k_2}(1 - e^{-kt})$$

Similarly $[C]_t = \frac{k_2[x]_0}{k_1 + k_2}(1 - e^{-kt})$

$[B]_t + [C]_t = [y] + [x]$

$$= \frac{k_1[x]_0}{k}(1 - e^{-kt}) + \frac{k_2[x]_0}{k}(1 - e^{-kt})$$

$$= \left(\frac{k_1 + k_2}{k}\right)[x]_0(1 - e^{-kt}) = [x]_0\ e^{(1-e^{-kt})}$$

$$\therefore \frac{[x]_t}{[y] + [2]} = \frac{e^{-kt}}{1 - e^{-kt}} = \frac{1}{e^{+(k_1+k_2)t} - 1}$$

Sol.20 [C] Using results of previous question

$[C]_t = \frac{k_2[A]_0}{k}(1 - e^{-kt})$, $k = k_1 + k_2$

$[A]_t = [A]_0e^{-kt}$

$$\frac{[C]_t}{[A]_t} = \frac{k_2}{k_1 + k_2}\frac{(1 - e^{-kt})}{e^{-kt}} = \frac{1}{1 + \frac{k_1}{k_2}}(e^{-kt} - 1)$$

We have, $k_1 = x\ \text{hr}^{-1}$, $k_2 = 10\ k_1$

$= 10 \times \text{hr}^{-1}$, t = 1 hr

$$\therefore \frac{[C]_t}{[A]_t} = \frac{1}{1 + \frac{1}{10}}(e^{(x+10x)} - 1)$$

$$\frac{[C]_t}{[A]_t} = \frac{10}{11}(e^{11x} - 1)$$

Paragraph-1

Sol.21 [B] Total number of moles

$= 1 + \frac{2}{3} + \frac{4}{3} = 3$ moles

Sol.22 [C] Moles of B $= \frac{2}{3} = 0.\ 666$ moles.

Paragraph-2

Sol.23 [B] We have,

$n_1A(g) \to n_2B(g)$

time 0 a 0

time t $a - n_1x$ n_2x

$\therefore$ Rate $= k[A] = \frac{-1}{n_1}\frac{d[A]}{dt} = k[A]$

$$\Rightarrow \int_a^{a_t}\frac{d[A]}{dt} = -n_1k\int_0^t dt$$

$$\ell n\frac{a_t}{a} = -n_1kt$$

$a_t = a\,e^{-n_1kt}$

Sol.24 [D] $n_1A(g) \to n_2B(g)$

t = 0 a 0

t = 1 $a\,e^{-n_1kt}$ $\frac{n_2}{n_1}a(1 - e^{-n_1kt})$

Total moles present

$$= a\left[e^{-n_1kt} + \frac{n_2}{n_1} - \frac{n_2}{n_1}e^{-n_1kt}\right]$$

$$= a\left(\frac{n_2}{n_1} - \left(\frac{n_2}{n_1} - 1\right)e^{-n_1kt}\right)$$

Concentration is to remain same at time t,

$$\therefore \frac{\text{total moles present}(n)}{V} = \frac{a_0}{V_0}$$

$$\Rightarrow V = \frac{V_0\,n}{a_0} = V_0\left[\frac{n_2}{n_1} - \left(\frac{n_2}{n_1} - 1\right)e^{-n_1kt}\right]$$

Sol.25 [B] If $n_1 = 1$, $n_2 = 2$

at time t,

$n_A = ae^{-kt}$

$V = V_0(2 - (2 - 1)e^{-kt})$

$= V_0(2 - e^{-kt})$

$$[A] = \frac{n_A}{V} = \frac{ae^{-kt}}{V_0(2-e^{-kt})} = [A]_0\left(\frac{e^{-kt}}{2-e^{-kt}}\right)$$

Paragraph-3

Sol.26 [C] $[B] = \frac{k_1[A]_0}{k_2-k_1}[e^{-k_1t} - e^{-k_2t}]$

$$\frac{d[B]}{dt} = \frac{k_1[A]_0}{k_2-k_1}(-k_1e^{-k_1t} + k_2e^{-k_2t})$$

When [B] is maximum, $\frac{d[B]}{dt} = 0$

$$\frac{d[B]}{dt} = 0$$

$$\Rightarrow -k_1e^{-k_1t} + k_2e^{-k_2t} = 0$$

$$k_1e^{-k_1t} = k_2e^{-k_2t}$$

$$e^{(k_1-k_2)t} = \frac{k_1}{k_2}$$

$$(k_1 - k_2)t = \ln\frac{k_1}{k_2}$$

$$\Rightarrow t = \frac{1}{k_1-k_2}\ln\frac{k_1}{k_2}$$

Sol.27 [C] For $k_1 = 1000\ s^{-1}$, $k_2 = 20\ s^{-1}$,

$[A]_t = [A]_0\, e^{-1000t}$

$$[B]_t = \frac{1000}{20-1000}[A]_0[e^{-1000t} - e^{-20t}]$$

$$\approx [A]_0e^{-20t},\ t_{max} = \frac{1}{1000-20}\ell n\frac{1000}{20}$$

$[B]_t$ will increase till t_{max} and then decay exponentially

$[C]_t = [A]_0 - ([A]_t + [B]_t)$

$= [A]_0 - [A_0]\, e^{-1000t} - [A]_0e^{-20t}$

$= [A]_0(1 - e^{-1000t} - e^{-20t})$

$\approx [A]_0(1 - e^{-20t})$

$[C]_t$ will approach $[A]_0$ asymptotically.

Sol.28 (A)S

We have,

$$\frac{1}{2}\frac{d[B]}{dt} = \frac{-d[A]}{dt}$$

Straight line with slope equal to 2.

(B)R

$[A] = [A]_0e^{-kt}$

exponential decay

(C)P

$[B] = 2([A]_0 - [A])$

$= 2[A]_0(1 - e^{-kt})$

Exponential graph will approach $2[A]_0$ asymptotically.

(D)Q

For zero order,

$[A] = [A]_0 - kt$

Straight line with slope –k.

Sol.29 We will draw all graphs given in Column-II and then match them with Column-I.

(P)ln[A] vs t (order 1)

We have, $[A] = [A]_0e^{-kt}$

$\ln[A] = \ln[A]_0 - kt$

Straight line with negative slope matches (A).

(Q)$t_{1/2}$ vs $[A]_0$ (order = 1)

$$t_{1/2} = \frac{0.693}{k}$$

It is independent of $[A]_0$, straight line parallel to x-axis. Matches (B)

(R)r vs t (order > 0)

$r = k[A]^n,\ n > 0$

for order > D, rate decreases with increasing t as [A] decreases with t

∴ decreasing graph (not straight line) matches (C).

(S)r vs t (order = 0)

For order, r is constant of time, graph is straight line parallel to x-axis.

(T)$t_{1/2}$ vs $[A]_0$ (order > 1)

We know,

$$t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$$

decreasing graph

Matches (C).

(U)$\frac{1}{[A]}$ vs t(order = 2)

we have,

$$\frac{-d[A]}{dt} = \frac{-k}{[A]^2}$$

$$\Rightarrow \int_{[A]_0}^{[A]}\frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$\Rightarrow \frac{-1}{[A]_0}\Bigg|_{[A_0]}^{[A]} = -kt\Big|_0^t$$

$$\Rightarrow \frac{1}{[A]_0} - \frac{1}{[A]} = -kt$$

$$\Rightarrow \frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Straight line with positive slope and positive intercept.

Matches no option in Column-I.

(V)r vs [A] (order = 1)

r = k[A]

Straight line with positive slope.

Matches (D)

(A) → P
(B) → Q, S
(C) → R, T
(D) → V

PREV YEARS' QUESTIONS JEE ADVANCED

Sol.1 The rate constant (k) of all chemical reactions depends on temperature.

$k = Ae^{-E_a/RT}$

where, A = Pre-exponential factor,

E_a = Activation energy.

Sol.2 A catalyst increases the rate of reaction but by the same factor to both forward and backward directions. Hence, a catalyst shorten the time required to reach the equilibrium.

Sol.3 Rate will be directly proportional to both concentration and intensity, i.e, rate of formation of AB * ∝ C. I.

Sol.4 Order of a reaction can take any real value, i.e, negative, integer, fraction, etc.

Sol.5 According to Arrhenius equation, rate constant increases exponentially with temperature :

(a) $k = Ae^{-E_a/RT}$

Sol.6. Living plants maintain an equilibrium between the absorption of C^{14} (produced due to cosmic radiation) and the rate of decay of C^{14} present inside the plant. This gives a constant amount of C^{14} per gram of carbon in a living plant.

Sol.7 . Fossil whose age is closest to half-life of C–14 (5770 yr) will yield the most accurate age by C–14 dating.

Sol.8 . $\lambda T = \ln\frac{N_0}{N}$

where N_0 = Number of C^{14} in the living matter and N = Number of C^{14} in fossil. Due to nuclear explosion, amount of C^{14} in the near by area increases. This will increase N_0 because living plants are still taking C–14 from atmosphere, during photosynthesis, but N will not change because fossil will not be doing photosynthesis.

⇒ T (age) determined in the area where nuclear explosion has occurred will be greater than the same determined in normal area.

Also, $\lambda T_1 = \ln\frac{C_1}{C}$

$\lambda T_2 = \ln\frac{C_2}{C}$

$\Rightarrow T_1 - T_2 = \ln\frac{C_1}{C_2}$

C = Concentration of C–14 in fossil.

Sol.9 (0)

Rate of reaction is constant with time.

Sol.10 $k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5770}\ yr^{-1} = 1.2 \times 10^{-4}\ yr^{-1}$

Also $kt = \ln\frac{1}{f} = \frac{\ln 2}{5770} \times 11540$

$= \ln 4$

$\Rightarrow f = \frac{1}{4} = 0.25$

Sol.11 $k = 1.5 \times 10^{-6}\ s^{-1}$

$kt = \ln\frac{100}{100-x}$

$\Rightarrow \ln\frac{100}{100-x}$

$= 1.5 \times 10^{-6}\ s^{-1} \times 10 \times 60 \times 60 s$

$= 0.0054$

$\Rightarrow \frac{100}{100-x} = 1.055$

⇒x =5.25% reactant is converted into product

Half-life $= \frac{\ln 2}{k} = \frac{0.693}{1.5 \times 10^{-6}} = 462000$ s

= 128.33 h

Sol.12 The minimum rate of decay required after 6.909 h is 346 particles min^{-1}.

⇒Rate = kN

$\Rightarrow N = \frac{Rate}{k} = \frac{346 \times 66.6 \times 60}{0.693}$

$= 1.995 \times 10^6$ atoms

$\Rightarrow kt = \ln\frac{N_0}{N}$

$\Rightarrow \frac{\ln 2}{66.6} \times 6.909 = \ln\frac{N_0}{N} = 0.0715$

$\Rightarrow \frac{N_0}{N} = 1.074$

$\Rightarrow N_0 = 1.074 \times N = 1.074 \times 1.995 \times 10^6$

$= 2.14 \times 10^6$ atoms of Mo

$\Rightarrow$ Mass of Mo required

$= \frac{2.14 \times 10^6}{6.023 \times 10^{23}} \times 99 = 3.56 \times 10^{-16}$g

Sol.13 $CH_3–O–CH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$

At 12 min :$0.40 - p$ $\quad p \quad p \quad p$

Total pressure $= 0.4 + 2p$

Also $k \times 12 = \ln \frac{0.40}{0.40 - p}$

$= \frac{\ln 2}{14.5} \times 12 = 1.77$

$\Rightarrow p = 0.175$

$\Rightarrow$ Total pressure $= 0.4 + 2p$

$= 0.4 + 2 \times 0.175$

$= 0.75$ atm.

Sol.14 (a)$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

$\Rightarrow \ln\left(\frac{4.5 \times 10^7}{1.5 \times 10^7}\right) = \frac{E_a}{8.314}\left(\frac{50}{323 \times 373}\right)$

$\Rightarrow E_a = 22$ kJ

Also $\ln k = \ln A - \frac{E_a}{RT}$

At 50°C :

$\ln A = \ln(1.5 \times 10^7) - \frac{22 \times 1000}{8.314 \times 323} = 8.33$

$\Rightarrow A = 4.15 \times 10^3\ s^{-1}$

(b)$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

$600–p \qquad 2p \qquad \frac{p}{2}$

Total pressure $= 690 = 600 + \frac{3}{2}p$

$\Rightarrow p = 240$ mm

$\Rightarrow$ Partial pressure of $N_2O_5(g)$ remaining

$= 600 - 240$

$= 360$ mm

$\Rightarrow$ Mole-fraction $= \frac{360}{960} = 0.375$

Sol.15 (a)Partial pressure becomes half of initial in every 100 min, therefore, order = 1.

(b) $k \times 100 = \ln \frac{800}{400} = \ln 2$

$\Rightarrow k = 693 \times 10^{-3}\ \text{min}^{-1}$

(c) For 75% reaction; time required

= 2 × half-life

= 200 min

(d) $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

$800–x \qquad \frac{3}{2}x \qquad x$

Total pressure $= 800 + \frac{3}{2}x$

Also $800 - x = 700$

$\Rightarrow x = 100$

$\Rightarrow$ Total pressure

$= 800 + \frac{3}{2} \times 100 = 950$ mm

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